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الجامعة الأردنيـــة
كلية الدراسات العليا

التاريـــخ: ١٧ / ٥ / ٢٠١١

نموذج رقم (١٨)
اقرار والتزام بالمعايير الأخلاقية والأمانة العلمية
وقوانين الجامعة الأردنية وأنظمتها وتعليماتها
لطلبة الماجستير

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عنوان الرسالة: Stripping and hydrodynamic Analysis of ionic species at DB-18C6 modified platinum electrode

اعلن بأنني قد التزمت بقوانين الجامعة الأردنية وأنظمتها وتعليماتها وقراراتها السارية المفعول المتعلقة باعداد رسائل الماجستير عندما قمت شخصيا" باعداد رسالتي وذلك بما ينسجم مع الأمانة العلمية وكافة المعايير الأخلاقية المتعارف عليها في كتابة الرسائل العلمية. كما أنني أعلن بأن رسالتي هذه غير منقولة أو مستلة من رسائل أو كتب أو أبحاث أو أي منشورات علمية تم نشرها أو تخزينها في أي وسيلة اعلامية، وتأسيسا" على ما تقدم فانني أتحمل المسؤولية بأنواعها كافة فيما لو تبين غير ذلك بما فيه حق مجلس العمداء في الجامعة الأردنية بالغاء قرار منحي الدرجة العلمية التي حصلت عليها وسحب شهادة التخرج مني بعد صدورها دون أن يكون لي أي حق في التظلم أو الاعتراض أو الطعن بأي صورة كانت في القرار الصادر عن مجلس العمداء بهذا الصدد.

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STRIPPING AND HYDRODYNAMIC ANALYSIS OF IONIC SPECIES AT DIBENZO-18-CROWN-6 ETHER MODIFIED PLATINUM ELECTRODE

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This Thesis was Submitted in Partial Fulfillment of the Requirements for the Master's Degree in Chemistry

Faculty of Graduate Studies
The University of Jordan

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Committee Decision

This Thesis (Stripping and hydrodynamic analysis of ionic species at dibenzo-18-crown-6 ether modified platinum electrode) was successfully defended and approved on 5 /May/2011

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Dedication

To my dear mother, father, brothers and sisters

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List of Contents

List of Tables

List of Figures

List of Abbreviations

Dibenzo-18-crown-6	DB 18C6
Chemically modified electrodes	CMEs
Cyclic voltammetry	CV
degree of coverage	θ
Carbon paste electrode	CPE
Rotating disk electrode	RDE
Anodic Stripping Voltammetry	ASV
Poly(tetrafluoroethylene)	PTFE
High Performance Liquid Chromatography	HPLC

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Abstract

Voltammetric investigations on dibenzo-18-crown-6 (DB18C6)-coated platinum electrodes; stationary and rotating disk electrode (RDE) revealed their remarkable inertness towards molecular adsorption, which means suppression of surface processes and interferences. In the present work, DB-18C6–coated platinum electrodes were prepared at open-circuit conditions. The crown ether adsorb chemically intact in a limited potential region between 500 and -250 mV vs. Ag/AgCl. The chemical stability and surface coverage of (DB18C6) has been studied at polycrystalline stationary platinum and RDE electrodes in 0.5 M H_2SO_4 by cyclic voltammetry at room temperature. Electroanalysis of Cu^{2+}, Ag^{+} by the two electrodes showed the existence of a linear relationship between the peak current and the concentrations of these ions, while the RDE was more sensitive to smaller concentration in the range of 10^{-6} M, compared to the stationary one. Also the DB 18C6-coated rotating disk platinum electrode was used to study the relationship between the peak current and angular velocity $\omega^{1/2}$ of these two metals. A good linear relationship was obtained between the peak current and the $\omega^{1/2}$ of silver and copper respectively.

Polycrystalline platinum electrode was used for stripping analysis of Cu^{2+}, Ag^{+} ions. A good linear relationship between the deposition time and peak current are obtained. In addition the modified Pt electrode was used for stripping analysis of Ag^{+} ions. An excellent linearity between the stripping peak current and the concentrations of these ions was obtained in the range of 5×10^{-12} - 5×10^{-17} M with a regression coefficient of 0.9952. Stripping analysis of Cu^{2+} , Ni^{2+} and Cd^{2+} ions showed An excellent linearity between the stripping peak current and the concentrations of these ions in the range of 5×10^{-11} - 5×10^{-15} M with a regression coefficient of 0.989, 0.9931 and 0.9877 respectively. Anodic stripping voltammetry shows that the Pt electrode modified with DB18C6 was sensitive towards metal ions. The proposed electrode shows good operating characteristics such as sensitivity, selectivity and wide linear working range.

Validity of the stripping method was compared with AAS for determination of the concentration of copper ions in an alloy sample, and there is an excellent agreement between the two methods.

1. Introduction

1.1 An overview on the electrochemistry of metals electrodes

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential, or charge and their relationship to chemical parameters. In contrast to many chemical measurements, which involve homogenous bulk solutions, electrochemical processes take place at the electrode-solution interface.

There are many noble metals that are used as electrodes; such as gold, palladium, silver, mercury and platinum. But Platinum and gold are the most widely used metallic electrodes this is due to the fact that these electrodes offer very favorable electron transfer kinetics and a large anodic potential range. In contrast, the low hydrogen overvoltage at these electrodes limits the cathodic potential window (to the range of – 0.2→ – 0.5 V, depending on the pH of the supporting electrolyte system).

Although, mercury is a suitable choice as an electrode material because of its high hydrogen overvoltage that extends the cathodic potential window compared to platinum, it has many disadvantages; Mercury for instance has a limited anodic potential range due to oxidation of mercury and its toxity (Wang, 2006).

There was a historical belief that the platinum electrode is totally inert and involves only the pure metal as a surface, but during the past decades it has become evident that platinum electrodes are not as inert as believed. Platinum like many other noble metal electrodes has a tendency to form an oxide surface which changes the electronic, catalytic and crystallography of the surface. Nonetheless, platinum

electrode continues to find applications as an inert electrode for metallic electrodes potentiometry and conductivity measurements.

Moreover, Platinum adsorbs hydrogen readily and the amount of adsorbed hydrogen can be used to estimate the real surface area of platinum surface. On the other hand, Gold does not appreciably adsorb hydrogen and this factor together with its larger overpotential for hydrogen evolution makes gold the metal of choice for the study of cathodic processes. Platinum is used more often than are all other metals combined, because of its enhanced catalytic prosperities (Sawyer, *et al.*, 1995).

At sufficiently positive potentials, all the noble metals form an oxide film or layer of oxygen in aqueous solution with a fairly well-defined stoichiometry that can be used to estimate the real surface areas of the metals. This oxygen layer consists of chemisorbed oxygen with nucleation and growth of an oxide phase under severe anodic conditions (Sawyer, *et al.*, 1995).

The current-potential curve for platinum electrode in 0.5 M H_2SO_4 is shown in Figure 1.1, (Wang, 2006).

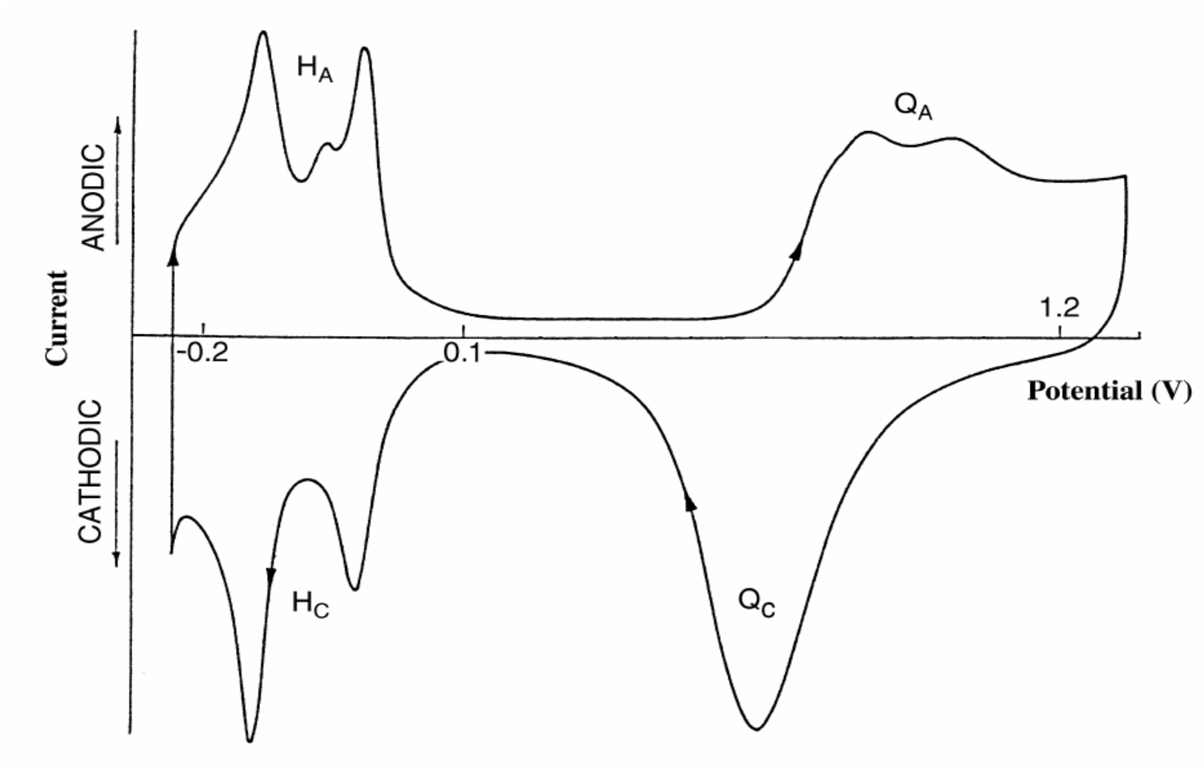


Figure 1.1 Cyclic voltammogram for platinum electrode in 0.5 M H_2SO_4

$\mathbf{H_A}$: oxidation of adsorbed hydrogen; $\mathbf{Q_A}$: formation of adsorbed oxygen or platinum oxide layer; $\mathbf{H_C}$: formation of adsorbed hydrogen; $\mathbf{Q_C}$: reduction of oxide layer.

1.2 Chemically modified electrodes

Chemically modified electrodes (CMEs) represent a modern approach to electrode systems, and has been very active one in recent years. These electrodes rely on the placement of a reagent onto the surface, to impart the behavior of that reagent to the modified surface. Such deliberate alteration of electrode surfaces can thus meet the needs of many electroanalytical problems, and may form the basis for new applications in electrochemistry. These electrodes may find many applications since the modified electrodes properties are different from those of unmodified ones; modified electrodes are prepared for a suitable function and purpose. Such surface functionlization of electrodes combined with molecular reagents has other applications, including energy conversion, electrochemical synthesis, and microelectronic devices (Wang, 2006).

The tailored design of electrode surface can serve the purpose of sensing, chemical recognition in analytical applications. The modifier serves the purpose of acceleration of electron transfer, preferential accumulation, which imparts higher sensitivity, selectivity, stability and increased rejection of impurities at electrochemical interfaces. In addition, many applications have been reported including; controlled release of drugs, electrosynthesis, fuel cells and corrosion protection (Wang, 2006). Adsorption on electrodes was the subject of many researchs during the 1960s and 1970s, so this area of research is now in its fifth decade and it has developed from the work of Anson and Moto in the 70s and 80s (Arrigan, 1994).

Chemically modified electrodes (CMEs) have been used to accumulate analytes selectively and to protect them from interference by other ions. CMEs consisting of

carbon paste and modifying reagent have been widely used, as they can be prepared readily and have stable response (Ijeri and Srivastava, 2000).

Modified electrodes can be prepared by different ways, including irreversible adsorption, covalent attachment, and coating the electrode with a film of polymer or other materials (Bard and Faulkner, 2001).

Polymer modification can place many monolayer's of active species on the CME surface. Various methods were used to prepare polymer-film electrodes, including: dip coating, oxidative or reductive deposition, electropolymerization, and spin coating (Arrigan, 1994).

1.2.1 Crown ethers as electrode modifiers

Crown ethers are macrocylic polyethers with the ability to "crown" cations. Their characteristic properties are their ability to solubilize ionic species in organic solvents, and thus increase the range of their reactivities. The size of the cavity available in each crown ether varies and determines the type of cation which is bound most efficiently. Their primary uses are the solubilization of inorganic compounds, separation of inorganic salts by use of the selectivity of various crown ethers, liquid-liquid extraction, liquid-membrane separation, ions elective electrodes, and organic synthesis as phase transfer reagents (Doxsee et al., 1993).

Since the pioneering work of Pedersen, 1967 and his devolpments on crown ethers, crown ethers and their complexes with metal cations have attracted much attention, which is not only because crown ethers are able to present unusual coordination numbers and arrangements on various metal ions but also because they act as models for metal ion transport across membranes (Dou et al., 2005).

Crown ethers (CE) developed by Pedersen are excellent hosts for alkali (M^{+}) and alkaline earth (M^{2+}) metal cations. They are widely applied in chemical technology and analytical chemistry as ion pair extractants, synergists, ion carriers, masking agents and sensors .The stability of cationic complexes, $[MCE]^{+}$ and/or $[MCE]^{2+}$, is mainly governed by the specific host–guest size match relationship between the diameters of macrocyclic ring of crown ether and of metal cations (Apostoluk et al., 2006).

The most recognizable member of crown ether family is 18- crown-6 and its benzo and dibenzo counterparts. Their complexation properties are well documented and most commonly studied **(** Piatek et al., 2009).

Electrodes modified with crown ethers have gained more importance in the last years and their major applications were in the area of metal analysis. Crown ethers have been used as modifiers for determination of lead, mercury, and other transition metals. DB-18 C6 has been used as modifier in carbon paste electrode for quantitation of copper by differential pulse voltammetry (DPV) (Ijeri and Srivastava, 2000).

The electrochemical behavior of pyridoxine hydrochloride (pyridoxine HCl) at the plain carbon paste electrode and the electrode modified with oxa crown ether has been studied using voltammetric and impedance measurements. The macrocycles used as modifiers were 18-crown-6, dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 and dibenzo-24-crown-8, out of which DB18C6 gave better response for pyridoxine HCl compared to other crown ether series (Desai et al., 2008).

Modification of electrode surfaces in general is of great interest for various applications. An interesting model for these modified electrodes is electrodes modified with crown ethers, because of the potential selective interaction between crown ethers and cationic moieties. 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and 40-amino-dibenzo-18-crown-6 (40-ADB18C6) have been investigated at single crystal and polycrystalline platinum surfaces in 0.5 M H_2SO_4 with differential electrochemical mass spectrometry (DEMS). The chemical stability and surface coverage of several adsorbed crown ethers have been reported (Bußar et *al*., 2005).

Wang and bonakdar, (1988). Reported preparation of Carbon-paste electrodes modified with crown-ethers. The electrodes so formed were able to bind mercuric ions chemically, and gave greater voltammetric response to mercury than that of Ordinary carbon-paste electrodes.

Preparation of membranes of dibenzo-24-crown-8 (I) as an ion active material in poly vinylchloride PVC was reported. These membranes were used for potentiometric analysis of zinc (II) (Gupta et *al*., 2005).

1.3 Cyclic voltammetry

Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions, and it's the first experiment performed in an electroanalytical study. It offers a rapid detection of electroactive species, and the reduction potentials of electroactive species, and convenient evaluation of the effect of media on the redox process (wang, 2006).

Cyclic voltammetry was first reported in 1938 and described theoretically by Randalls and Sevcik in 1948 (Nicholson, 1965; Christensen and Hamnett, 1994).

Cyclic voltammetry is an extension of linear sweep voltammetry with the potential applied is varied linearly between potentials E_1 and E_2, E_2 being a potential more positive (for oxidation) or negative (for reduction) than the peak maximum observed for the oxidation/reduction reaction concerned. At E_2 the voltage scan is reversed back to E_1 (Westbroek *et al.*, 2005).

The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics and reversibility of redox processes, the kinetics of heterogeneous electron transfer reactions and on coupled chemical reactions or adsorption processes (Holze, 2009).

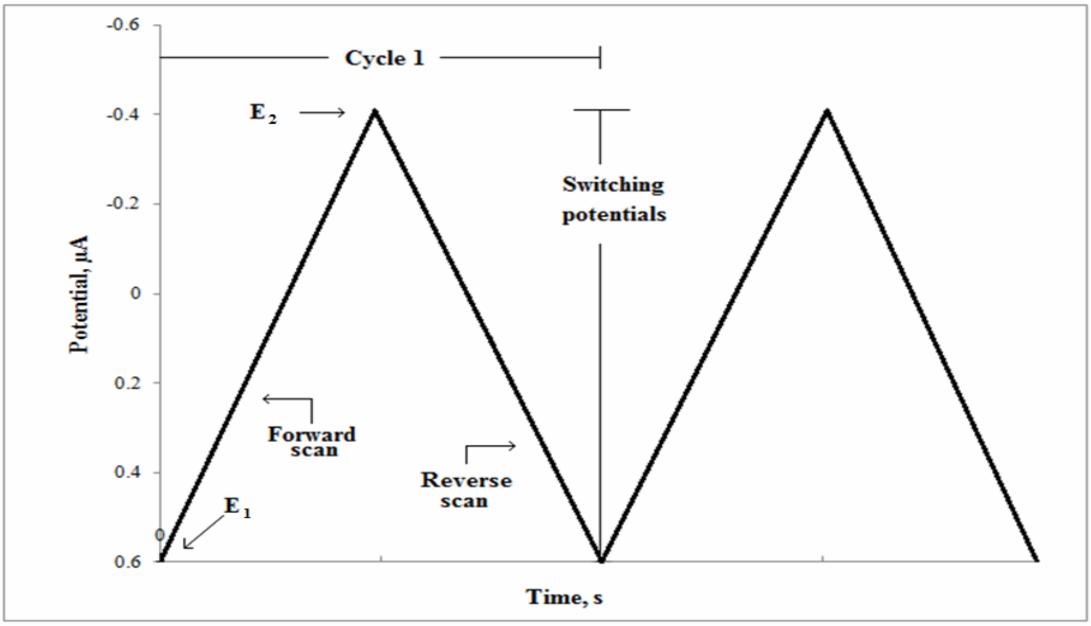


Figure 1.2 Potential-time excitation signal in cyclic voltammetric experiment

Cyclic voltammetry can also be used for surface characterization. The peak potential, multiplicities, relative intensities, and sharpness are indicators for the electronic state of the surface and their crystallographic orientations. Figure 1.3 illustrates the shape of a cyclic voltammogram with an electrode of fixed area. The voltammogram is characterized by a peak potential E_p, at which the current reaches a maximum value and by the value of the current i_p (Sawyer, et *al.*, 1995).

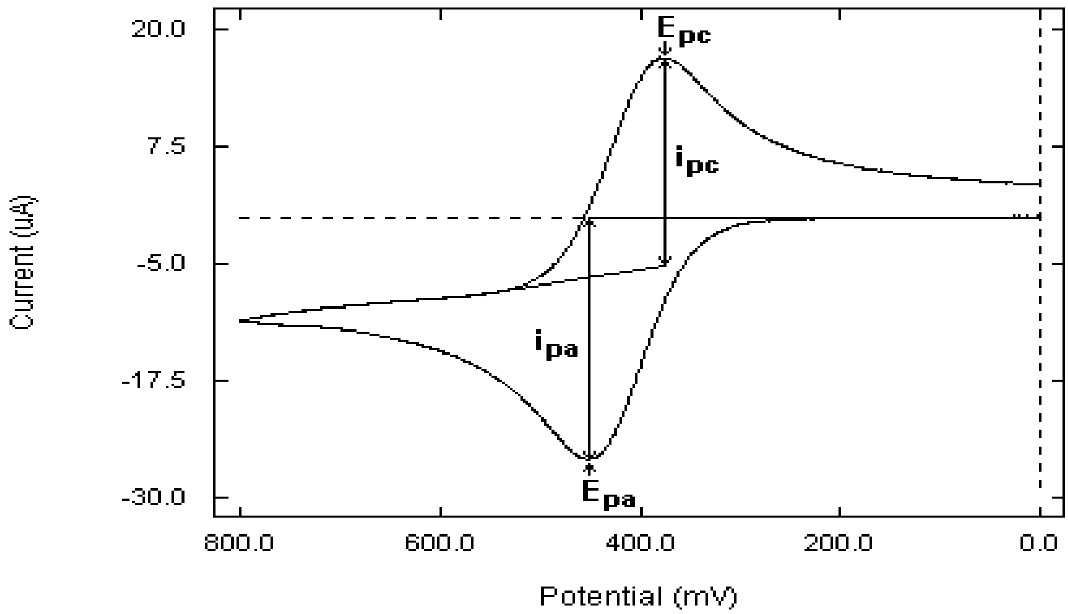


Figure 1.3 Typical cyclic voltammogram for a reversible reaction

i_{pc}* :** peak of cathodic current ; ***i_{pa} : peak of anodic current .

Cyclic voltammetry is also very useful for the study of adsorbed species, a distinction between reactions of species from solution and adsorbed species can be made by plotting the peak current as a function of scan rate. For species from solution, a square-root relation is obtained; for adsorbed species, a linear relationship is obtained. The charge can be calculated from the area under the peak (Westbroek et *al.*, 2005). Estimation of the degree of coverage (θ) of a platinum surface by adsorbate molecules is possible from the relation (Brad and Faulkner, 2001).

$$\theta = \left[1 - \frac{\text{area under hydrogen adsorption peaks in presence of adsorbate}}{\text{area under hydrogen peaks in absence of adsorbate}}\right]$$

1.4 Hydrodynamic techniques and Rotating disk electrode (RDE)

There are many electrochemical techniques for exploring the mechanisms of the electrochemical reactions. Among those, are the hydrodynamic electrode methods.

In these systems the electrode moves with respect to the solution, so that the electrode itself is in motion. Among the hydrodynamic electrode methods, the most convenient and widely-used systems are the rotating disc electrode (RDE) and rotating ring–disc electrodes (RRDE). These techniques are amenable to rigorous theoretical treatments and are easy to construct with a variety of electrode materials (Brad and Faulkner, 2001).

The advantages of hydrodynamic methods are that the steady-state diffusion is attained somewhat quickly and measurements can be made with high precision. In addition, the double-layer charges current approaches zero at steady-state due to the lack of change of potential with time, and hence the effect of the double-layer charging process on the overall reaction can be disregarded during the hydrodynamic measurements. Moreover, the rates of mass transfer at the electrode surface are typically larger than those rates associated with diffusion alone. Figure 1.4 shows a schematic representation of the RDE (Pyun et al., 2008).

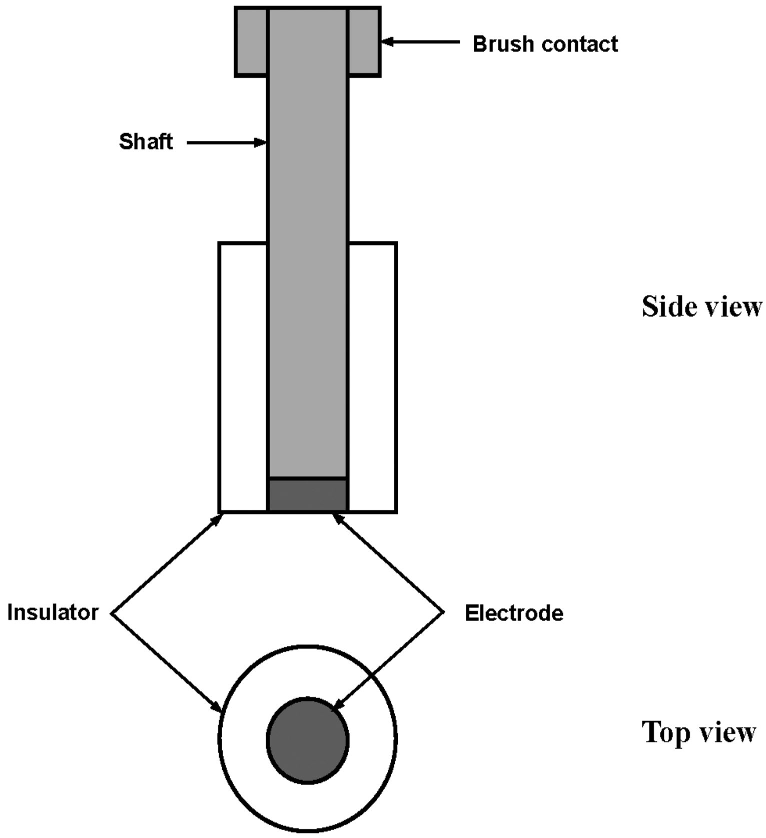


Figure 1.4 Schematic representation of a rotating disk electrode (RDE).

An adsorptive stripping voltammetric protocol coupled with a rotating-disk bismuth film electrode for the detection and speciation of chromium (ш) and chromium (VI) in the presence of diethylene-triaminepentaacetic acid (DTPA) is presented (Neto et al., 2010).

The speciation of lead and cadmium in model solutions of a well characterized fulvic acid (FA), Laurentian FA, was investigated by anodic stripping voltammetry (ASV) using a thin mercury film-rotating disk electrode (TMF-RDE) and a Nafion-coated TMF-RDE (Chakrabarti et al., 2000).

Eisner and co- workers (2000); reported a simple and highly reliable method for the determination of mercury on a rotating gold disk electrode. The signal is linear with concentration over a wide concentration range (0.2-400 nM) (Eisner et al., 2000).

Determination of bismuth (III) in sea water by square-wave anodic stripping voltammetry at a glassy-carbon rotating-disk electrode was reported by Lovric, 1988.

1.5 Stripping analysis:

Stripping analysis is a sensitive electrochemical technique for measuring trace metals. Its high sensitivity is attributed to the combination of preconcentration step with advanced analytical measurement that leads to a high S/N ratio. As the metals are preconcentrated onto an electrode by factors of 100-1000, detection limits are lowered by orders of magnitude compared to the linear sweep voltammetric measurements (Wang, 2006).

Stripping analysis is a two step technique, namely the deposition step which includes electrolytic deposition of small portions of the metal ions in solution into or at the electrode to preconcentrate the metal, followed by stripping of the deposit (measurement step). Anodic Stripping Voltammetry (ASV) and Cathodic Stripping Voltammetry (CSV) are two specific stripping techniques (Wang, 2006).

This technique is especially useful for the analysis of very dilute solutions (down to 10^{-10} to 10^{-11} M). Stripping analysis is more frequently used for the determination of metal ions by cathodic deposition, followed by anodic stripping with a linear potential scan and therefore, it's called anodic stripping voltammetry (ASV) (Bard and Faulkner, 2001).

Figure 1.5 illustrates potential time trace used in an anodic stripping volatammetry to determine the Copper and Cadmium concentrations.

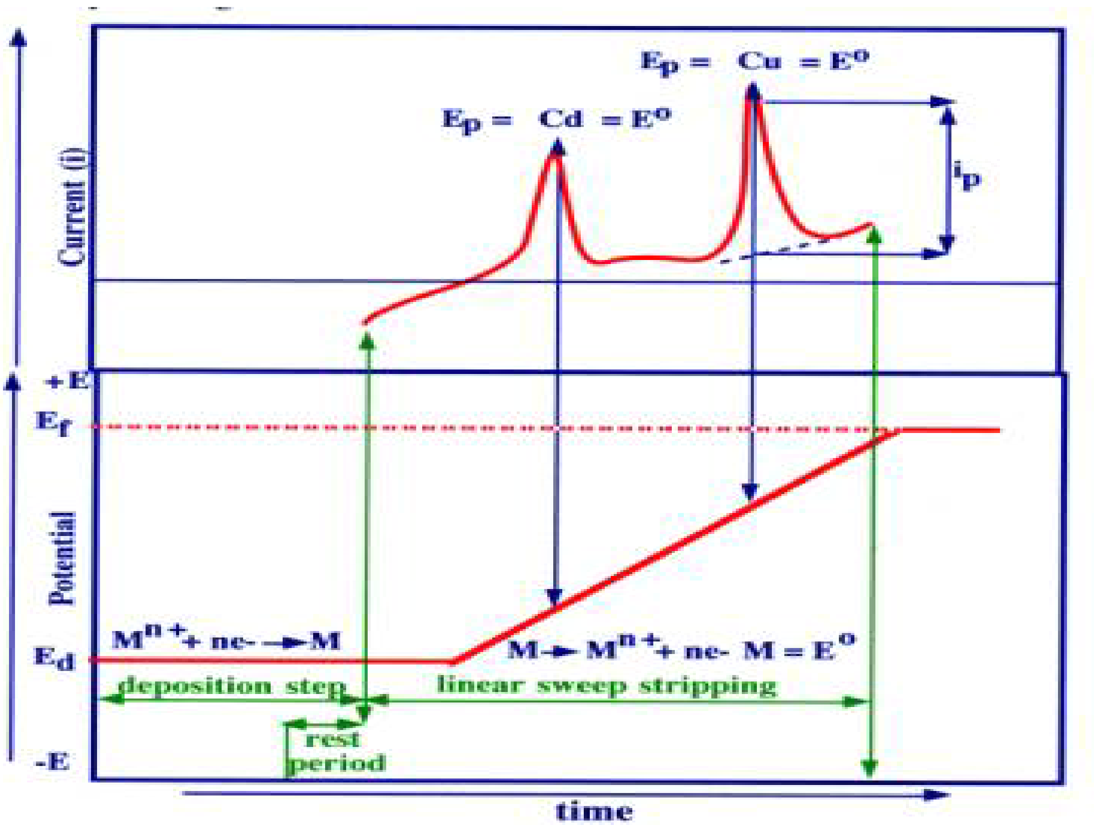


Figure 1.5 Potential time trace used in an anodic stripping voltammetry to determine the Copper and Cadmium concentrations.

The analytical instruments for stripping analysis are relatively simple and inexpensive, no additional instrumentation or analysis time is required for multi-element stripping measurements. Carbon paste electrode (CPE) chemically modified with phenylthiourea-nanoporous silica gel (Tu-SBA-CPE) was used for the determination of silver by anodic stripping voltammetry (ASV) (Javanbakht et al., 2009).

Iodine coated platinum electrode was utilized in stripping analysis of Ag (I).The stripping experiments involved a deposition step at -0.2 V in a stirred solution followed by an anodic linear potential scan in a quiescent solution (Hourani, 1999).

A mixed binder carbon paste electrode (MBCPE) containing dimethylglyoxime(DMG) system appropriate for the cathodic stripping voltammetric determination of mercury (II), cobalt (II), nickel (II) and palladium (II) (Zhang et al., 1996).

Pt-nanoparticles were synthesized and introduced into a carbon paste (CPE), and the resulting modified electrode was applied to the anodic stripping voltammetry of copper (II) ions (Won et al., 2007).

A carbon paste electrode modified with 2-mercapto-4(3H) - quinazolinone was used for the voltammetric determination of mercury (II). Mercury was preconcentrated onto the surface of the modified electrode only by the complexing effect of the modifier without application of potential (i.e. in open-circuit conditions). After exchange of the medium, the accumulated amount of mercury (II) was determined by differential pulse anodic stripping voltammetry (Kalcher et al., 1993).

1.6 Analysis of metals:

There are probably no materials that have shaped the progression of mankind more than metals. Several different types of metals exist in the environment. With the exception of metals such as gold, most metals have to be extracted from rock ore. Metal is so important in history of mankind because of its influence on industry. Copper makes up about 0.007 % of the earth's crust, making the 25 th most abundant element. Copper is one of the few elements that play an important technical role in the pure, non-alloyed state, mainly in the electrical industry. Because of its excellent heat conductivity, it's used for vacuum pans, soldering irons, stills, heating and cooling coils. Also it's an essential trace element for humans, higher mammals, and numerous plants. Copper is determined frequently by AAS (Welz and Sperling, 1999).

Silver is one of the rare elements; it is estimated that it makes up about 10^{-6} % of the earth's crust. Silver is the noble metal that is most heavily produced and used. Its uses include a coinage metal, in jewelry, photography, silver plating and for hard solders. Silver can be determined easily by flame AAS; the best characteristic concentration (detection limit) of 0.02 mg/L is obtained in the flame acetylene flame (Welz and Sperling, 1999).

Cadmium makes up about 5 $x10^{-5}$ % of the earth's crust and is thus one of the rare metals. Cadmium and numerous of its compounds are toxic. About a third of the Cd production is used in the manufacture of batteries; other applications include addition as anticorrosive for iron and other metals. The usage of Cd pigments and Cd soap as stabilizers for PVC. Cd can be easily atomized and thus determined without any

noteworthy interferences in the air-acetylene flame. For a long period the greatest difficulty for determining Cd by graphite furnace (GF) AAS was its high volatility, Lundgren et al, 1974 utilized this volatility to atomize Cd at 800 °C.

The proportion of Ni in the earth's crust is estimated to be 0.015 %; Ni is thus at position 22 in the abundance list of the elements. The greatest part of the production of Ni is used in the steel industry and for the production of alloys.

Ni is among the elements determined frequently by AAS; the best characteristic concentration of 0.04 mg/L is obtained in the flame acetylene flame (Welz and Sperling, 1999).

A new sensor was developed for simultaneous detection of cadmium (Cd^{2+}), copper (Cu^{2+}) and lead (Pb^{2+}), based on the voltammetric response at a carbon paste electrode modified with carbamoylphosphonic acid (acetamide phosphonic acid) self-assembled monolayer (SAM) on mesoporous silica (Ac-Phos SAMMS). The adsorptive stripping voltammetry (AdSV) technique involves preconcentration of the metal ions onto Ac-Phos SAMMS under an open circuit, then electrolysis of the preconcentrated species, followed by square wave potential sweep towards positive values (Lin et al., 2004).

A new functionalized nanoporous silica gel with dipyridyl group (DPNSG) was synthesized. Then, the potentiometric response of Cu^{2+} ion was investigated at a carbon paste electrode chemically modified with this newly designed functionalized nanoporous silica gel (Javanbakht et al., 2007).

Iodine- coated platinum electrode was used for the electroanalysis of Ag^{+}, Hg^{2+} and Fe^{3+} by voltammetry (Hourani et al., 1995).

A polypyrrole modified electrode loaded with pyrocatechol violet (PCV) was used for the extraction and then electroanalysis of copper species by anodic stripping differential pulse voltammetry. The logarithm of peak current was found to be linearly related to the logarithm of copper concentration (Bagheri et al., 1998).

PVC-membrane electrodes based on 18-crown-6 and Dibenzo-18-crown-6 ethers were applied for the potentiometric determination of silver (Ag^+) for the first time. The electrodes showed good selectivity towards most of the common alkali, alkaline earths, and transition metal cations. Several types of crown ether-metal were previously used to prepare Ag^+ -selective electrodes (Zareh et al., 2007).
Cadmium (II) selective sensors have been fabricated from poly (vinyl chloride) (PVC) matrix membranes containing neutral carrier, dibenzo-24-crown-8 as ionophore and dibutyl(butyl)phosphonate (DBBP), diphenylether (DPE) and 1- chloronaphthalene (1-CN) as plasticizing solvent mediators (Gupta et al., 1999).

1.7 Atomic absorption spectrometry and validation of the methods:

Atomic absorption spectrometry (AAS), which for nearly half a century has been the most widely used method for determination of single elements in analytical samples at a time (Skoog, 2007).

AAS well established in numerous fields of instrumental analysis. Due to its high specificity and selectivity, as well as the fact that operation is relatively simple.

It is used to perform numerous routine tasks in the laboratory ranging from the determination of trace contents through to major constituents. Because AAS is specific and exhibits great freedom from interferences, its range of applications is correspondingly large; including sample preparation, such as dissolution or digestion of solid samples, environmental analysis (water, soil, air), analysis of plants and animal feeding stuffs. Analysis of industrial products, geochemistry and prospecting (rocks, minerals, ores) and in metallurgical products.

Copper is determined frequently by AAS; it can be atomized relatively easily and exhibits no interferences in the air-acetylene flame (Welz and Sperling, 1999).

1.8 Importance and objectives of the present work

Hyper-reactivity of platinum bare electrodes poses a problem for their uses in routine chemical analysis. Modified platinum electrodes, however, show much lower reactivity and the modifiers of platinum electrodes might be tailored to improve their selectivity towards specific purposes in addition to reduction of the hyper-reactivity.

In the present work, dibenzo- 18-crown-6 ether will be used as a modifier. The selectivity of binding of crown ethers with the activity of noble metals will be utilized in the present work for the analysis of some metals. Hydrodynamic techniques, which are known of their high sensitivity, will be utilized for testing dibenzo-18-crown-6 platinum electrode.

The quest for simple analytical methods that do not rely on expensive instrumentation or novel procedures is an objective in research and development in analytical chemistry. Modified electrodes lend themselves to be used as basis for manufacturing of potentiometric and voltammetric sensors and herein comes the importance of this investigation.

The present work aims at achievement of the following objectives :

1. Modification of platinum electrode wire and rotating disk platinum electrode with dibenzo-18-crown-6 ether and the electrochemical characterization of the prepared electrodes surfaces.
2. Application of the modified rotating disk platinum electrode for analysis of silver and copper ions in aqueous solutions, and investigation of the cyclic voltammetric response of it towards metal ions.
3. The applicability of the modified platinum electrode will be tested towards silver and copper ions in aqueous solution.

4. Application of the prepared platinum electrode for stripping analysis of silver,copper, cadimum and nickel ions in aqueous solutions.

5. Validation of the method by comparision with AAS.

2. Experimental

2.1 Electrodes

A classical three-electrode cell was used for cyclic and hydrodynamic voltammetric measurements, these are working electrode (at which the reaction of interest occurs), reference electrode (it provides a stable fixed potential independent of the sample composition against which the potential of the working electrode was compared); and a platinum auxiliary electrode was used to complete the current path and to avoid loading the reference electrode.

The cell comprised of tow inlet/ outlet system which allowed admission of the supporting electrolyte, purging and blanketing the solution with oxygen-free nitrogen. Residues of oxygen were removed from nitrogen by coupling the ultrapure nitrogen gas cylinder supplied by International Gas Company (purity 99.99%, Amman-Jordan) to an oxisorb cartridge (Supelco, USA).

Purging with an inert gas (usually purified nitrogen or argon) for 4-8 minutes prior to recording the voltammogram was carried out before every experiment. The purging gas was allowed to pass through a bubbler for washing before allowing the gas to pass through the other bubblers and the cell. Large sample volume for the rotating disk platinum electrode required longer purging time. To prevent oxygen from reentering the cell, the cell should be blanketed with the gas while the voltammogram was recorded.

The purged supporting electrolytes were dispensed from bubblers into the electrochemical cell by gravity action. All the tubes used for purging with nitrogen or used for conveying solutions to the cell were made of 1/16" I.D PTFE (Cole Parmer, USA).

The reference and auxiliary electrodes were immersed in one compartment, while the working electrode was placed in the other compartment (Figure 2. 1).

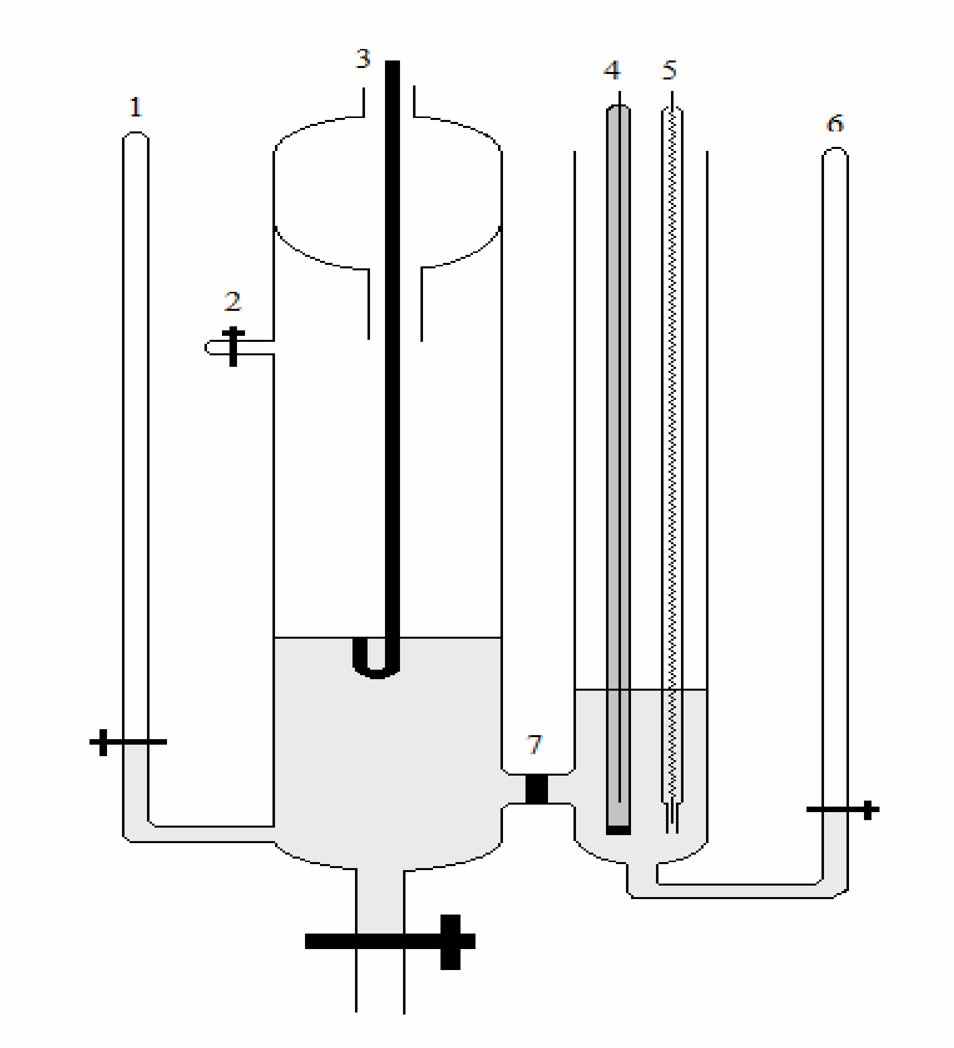


Figure 2.1 Three electrode cell setup

1: Purging inlet, 2: Blanketing inlet, 3: Working electrode, 4: Reference electrode, 5: Auxiliary electrode, 6: Purging inlet, 7: porous frit

Two kinds of working electrodes were used, a stationary platinum electrode and hydrodynamic rotating-disk platinum electrode. An Ag/AgCl/[Cl^-]=1.0 M reference electrode was constructed using a silver wire coated with silver chloride by an electrochemical procedure. Where all the reported potentials were referenced to this electrode. A platinum spiral wire (99.99 % purity, Johnson Matthey, USA) fitted in a glass tube was used as an auxiliary electrode.

In the working electrode, the tip was of a polycrystalline platinum wire; 1.0 mm, 99.99% purity, (Johnson Matthey, USA), rounded at the end to produce a reproducible surface area upon immersion underneath the surface of the solution in the working electrode compartment. The rotating disk platinum electrode (Pine instrument Company, USA) was made of platinum disk imbedded in a PTFE sleeve. The rod was attached to a motor by a flexible shaft, which allows rotation at a certain speed ranging from 1 to 9999 revolutions per minute (rpm). The most useful descriptor of rotation rate is the angular velocity, ω (s^{-1}), where $\omega = 2\pi f$ (f is the rotation speed in rps (revolutions per second)). Figure 2.2 shows a schematic diagram for the rotating disk platinum cell

All experiments were carried out in deoxygenated aqueous solutions.

2.2 Materials and Instrumentation

All chemicals used were of analytical grade quality supplied by different companies and used as received without further purification.

Potassium Chloride (Scientific limited, England), Nitric acid (Merck, Germany), Crown ether; dibenzo-18-crown-6 (DB18C6) was obtained from Merck chemicals, (USA).

Silver perchlorate hydrate, 99 % purity and copper perchlorate hexahydrate, 98% purity (Acros organics, USA) where perchlorate salts were chosen here because it doesn't make any complexation with metals. Cadmium oxide from (Merck, USA) and nickel sulfate from (Gainland chemical company, U.K).

Sulfuric acid was used as supporting electrolyte (0.5 M) from (Merck, USA).

All glassware used in this work were cleaned with chromic acid solution and washed with triply distilled water that was also used for preparing all the solutions in this work. The triply distilled water prepared by three-stage distillation where the second one was distilled from potassium permanganate to destroy any organic impurities.

Cyclic voltammetric and linear scan experiments were obtained using (EG & G model 362) Scanning potentiostat (Princton Applied Research, USA). The potentiostat was interfaced to a computer through GPIB card (IEEE) with modified labview software.

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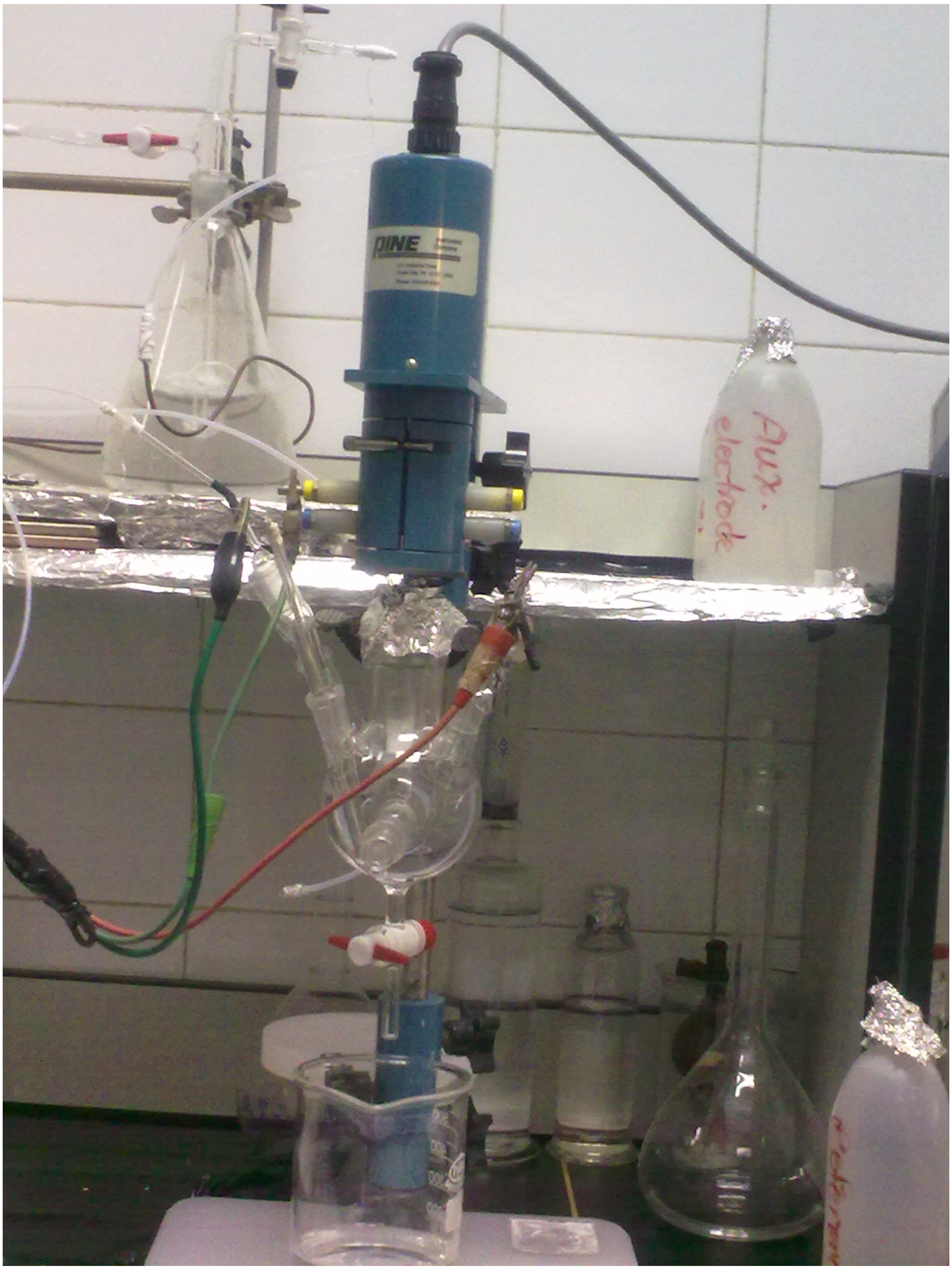


Figure 2.2 Rotating disk platinum electrode cell.

2.3 Experimental procedure

2.3.1 Surface pretreatment

Surface pretreatment is the first procedure that must be used before anything else, and It's an essential one. For platinum the electrode surface was polished with alumina powder, immersed in concentrated hydrofluoric acid to remove any alumina traces, then dipped for 5-10 minutes in a freshly prepared chromic acid solution and finally rinsed with triply distilled water. The electrode was placed in a cell containing 0.5 M H_2SO_4. The electrode was conditioned by cyclization of electrode potential between -0.25→1.3 V to remove any surface impurities and reproducing the regular cyclic voltammogram for the platinum electrode in 0.5 M H_2SO_4. Thus, each experiment was conducted on a verified-clean electrode.

For rotating platinum disk electrode, it was cleaned with chromic acid only followed by rinsing with triply distilled water to produce the clean surface. Also the RDE was conditioned by cyclization of electrode potential between -0.25→1.3 V, as in the case of the stationary electrode.

2.3.2 Modification of platinum electrode by adsorption of crown ether

The platinum electrode was modified by adsorption of DB-18C6 crown ether on its surface; Figure 2.3

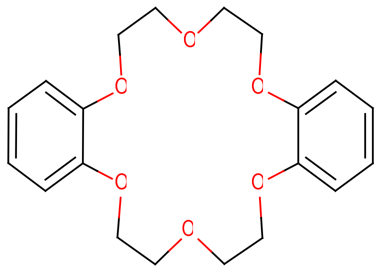


Figure 2.3 Structure of Dibenzo-18-Crown-6 (DB-18C6)

The platinum wire electrode was allowed to contact a solution of 1×10^{-3} M DB-18C6 for 20-30 minutes at open circuit with continuous stirring, then the electrode was rinsed extensively with triply distilled water, and replaced in the cell, which contained a purged 0.5 M H_2SO_4, and characterized by cyclic voltammetry. The crown ether was stable at a negative going potential scan from 0.5 to -0.25 V. The same procedure was used for rotating disk platinum electrode.

2.3.3 Analysis of copper and silver metals using the modified electrodes

Solutions of 1×10^{-4} - 6×10^{-4} M of Copper perchlorate solution was prepared in 0.5 M H_2SO_4.

The modified platinum wire electrode was replaced in the cell, which contained a purged 1×10^{-4} M Cu solution, a negative going potential scan from 0.5 to -0.25 V, was recorded.

The same procedure was used with other concentrations.

Solutions of 3×10^{-6}, 4×10^{-6}, 5×10^{-6}, 6×10^{-6} , 7×10^{-6}, 1×10^{-5}, 2×10^{-5}, 3×10^{-5} , 4×10^{-5} , 1×10^{-3} M of Cu perchlorate solution was prepared in 0.5 M H_2SO_4.

The modified rotating disk platinum electrode was replaced in the cell, which contained a purged 3×10^{-6} M Cu solution, a negative going potential scan from 0.5 to -0.25 V, was recorded.

The same procedure was used with other concentrations.

Solutions of 0.5×10^{-4} - 5×10^{-4} M of Silver perchlorate solution was prepared in 0.5 M H_2SO_4.

The modified platinum wire electrode was replaced in the cell, which contained a purged 0.5×10^{-4} M Ag solution, a negative going potential scan from 0.5 to -0.25 V, was recorded.

The same procedure was used with other concentrations.

Solutions of 3×10^{-6}, 4×10^{-6}, 5×10^{-6}, 6×10^{-6} , 7×10^{-6}, 8×10^{-6} ,1×10^{-5}, 2×10^{-5}, 3×10^{-5} , 4×10^{-5} , 5×10^{-5} M of Silver perchlorate solution were prepared in 0.5 M H_2SO_4.

The modified rotating disk platinum electrode was replaced in the cell, which contained a purged 3×10^{-6} M Ag solution, a negative going potential scan from 0.5 to -0.25 V, was recorded.

The same procedure was used with other concentrations.

2.3.4 Variation of peak current (i_p) with angular velocity ($\omega^{1/2}$) at a Rotating disk electrode for solutions of Cu and Ag.

A solution of 1×10^{-5} M of Silver perchlorate was prepared in 0.5 M H_2SO_4, then the relation between peak current (ip) and angular velocity ($\omega^{1/2}$) was investigated.

The $\omega^{1/2}$ values from 100 to 1500 rpm were studied.

The same procedure was used with 1×10^{-5} M Cu solution. The $\omega^{1/2}$ values from 100 to 900 rpm were investigated.

2.3.5 Anodic stripping analysis of Ag, Cu, Ni, and Cd solutions at a Modified platinum wire electrode

A solution of 5×10^{-7} M Ag was prepared in 0.5 M H_2SO_4. The silver ions were cathodically deposited onto the electrode surface at a (-0.25 V), and then its anodicaly stripped from the electrode surface.

Preconcentarion times from 5-35 minutes vs. peak current (ip) have been studied.

The same procedure was used with 5×10^{-9} M Ag solution. Preconcentration times of (5, 15, 25, 30, 35, 40, 45 minutes) vs. peak current (ip) have been studied.

The same procedure was used with 5×10^{-10} M Ag solution at Preconcentration times of (5, 10, 15, 30, 35, 40, 45 minutes) was investigated.

The same procedure was repeated with 5×10^{-11} M Ag solution at Preconcentration times of from 5 – 30 minutes.

Solutions of 5×10^{-12} – 5×10^{-17} M of Ag were prepared in 0.5 M H_2SO_4.

The modified platinum wire electrode was replaced in the cell, which contained a purged 5×10^{-12} M Ag solution, preconcentration time for 10 minutes at a negative potential (-0.25 V), then the metal was stripped at a positive potential (0.5 M).

The other concentrations were stripped in the same manner.

A solution of 5×10^{-5} M Cu was prepared in 0.5 M H_2SO_4. The Copper ions was cathodically deposited onto the modified electrode surface at a (-0.25 V), and then it was anodicaly stripped from the electrode surface.

Preconcentration times (5 – 35 minutes) vs. peak current (ip) have been studied.

Solutions of 5×10^{-11} – 5×10^{-15} M of Cu were prepared in 0.5 M H_2SO_4.

The modified platinum wire electrode was replaced in the cell, which contained a purged 5×10^{-11} M Cu solution, preconcentration time for 10 minutes at a negative potential (-0.25 V), then the metal was stripped by a positive potential scan to 0.5 V. The other concentrations were treated in the same manner.

Solutions of 5×10^{-11} – 5×10^{-15} M of nickel and cadmium were treated in the same way.

2.3.6 Determination of the Cu concentration in a brazing alloy Sample by AAS

A 0.50 g of a brazing alloy sample (Degussa Company, Germany) was dissolved in a small volume of nitric acid, after that it was diluted with water to 850 mLs in a different volumetric flasks.

From 1000 ppm Cu standard solution, four samples (2.5, 5, 10, 20 ppm) were prepared and analyzed by AAS with the brazing alloy sample.

The concentration of Cu in the alloy sample and its concentration by stripping analysis were compared.

3. RESULTS AND DISSCISION

3.1 Validation of cleanliness and voltammetric characteristic of polycrystalline platinum electrodes

Each experiment was commenced by reproducing the cyclic voltammogram of the clean electrode. The cyclic voltammogram is the electrochemical spectrum through which surface cleanliness and the surface states are characterized. Cyclic voltammogram also provides the tools for calculation of real surface area.

3.1.1 Polycrystalline platinum wire and rotating disk platinum electrodes

The cyclic voltammograms of polycrystalline platinum wire and rotating disk platinum electrodes are given in Figure 3.1 and Figure 3.2 respectively.

Figure 3.1 shows cyclic voltammogram of a platinum wire electrode in 0.5 M H_2SO_4. The current–potential curve for platinum electrode shows the well-known peaks for hydrogen adsorption / desorption and the voltammetric characteristics for surface oxidation and desorption of oxygen.

Figure 3.2 shows cyclic voltammogram of rotating disk platinum electrode in 0.5 M H_2SO_4, same voltammetric features were similar to those observed in Figure 3.1. The difference in surface areas is noticed and estimated from areas under the peaks.

The area under hydrogen adsorption or hydrogen desorption peaks represents the charge for hydrogen adsorption and desorption respectively.

The real surface area of platinum electrode can be estimated from the charge needed to desorb hydrogen (210 $\mu C/cm^2$) (Brad and Faulkner, 2001).

Calculation of the real surface area is necessary for quantification of the adsorbed compounds at the surface of the electrode.

Quantitatively, the difference in hydrogen adsorption or desorption charges might be taken as a measure of the coverage of the surface with the adsorbed compounds. This method for calculation of coverage of the adsorbate is applicable when there is no interaction between hydrogen and the adsorbed compounds. If this condition is valid, then the coverage is calculated according to the following equation:

$$\theta = \left[1 - \frac{Q_{Ha}}{Q_{Hc}}\right]$$

Where Q_{Ha} corresponds to the charge for hydrogen adsorption in presence of the adsorbed species and Q_{Hc} corresponds to charge for hydrogen adsorption on clean electrode.

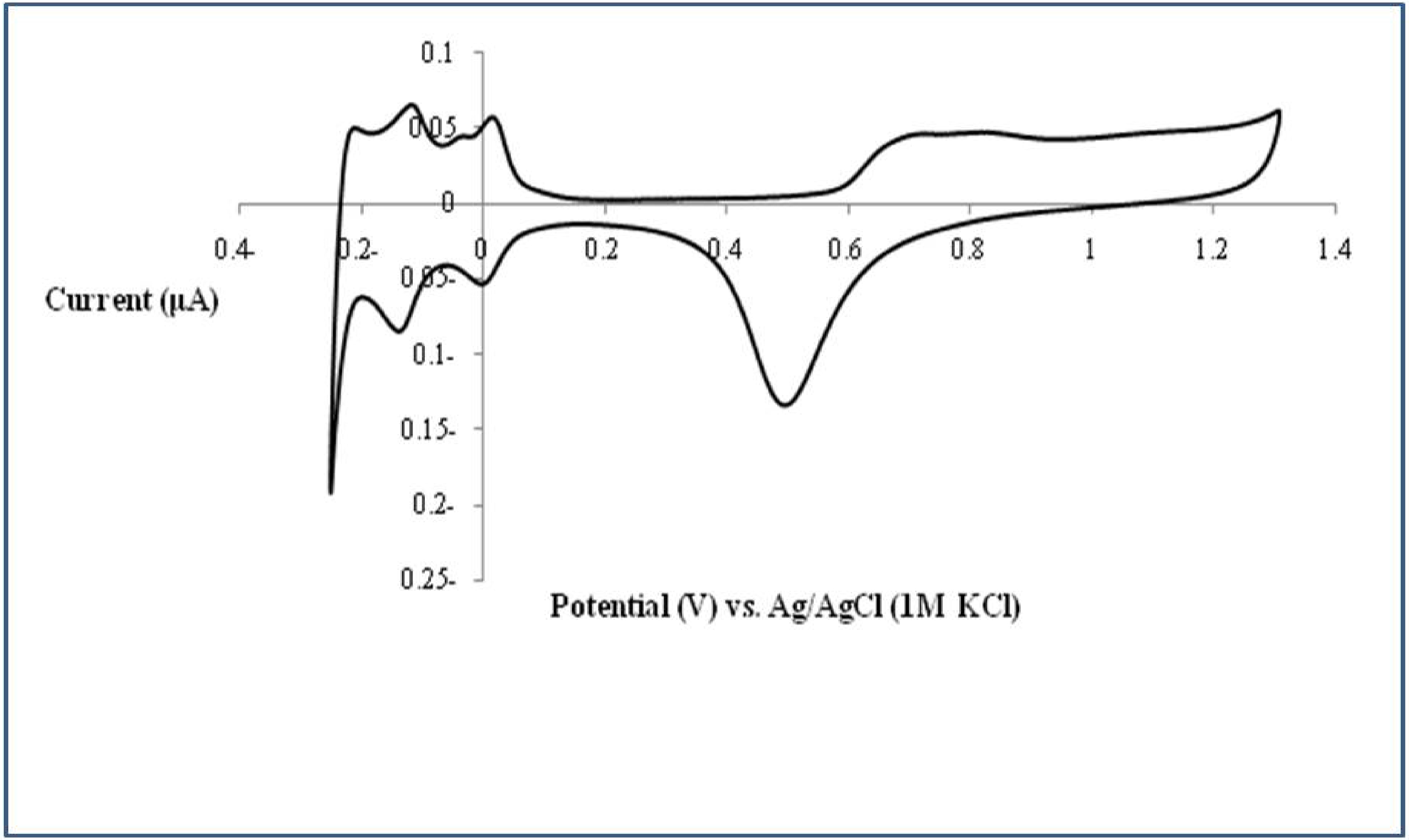


Figure 3.1 Cyclic voltammogram of a polycrystalline stationary platinum electrode in 0.5 M H_2SO_4 at scan rate 50mV/s

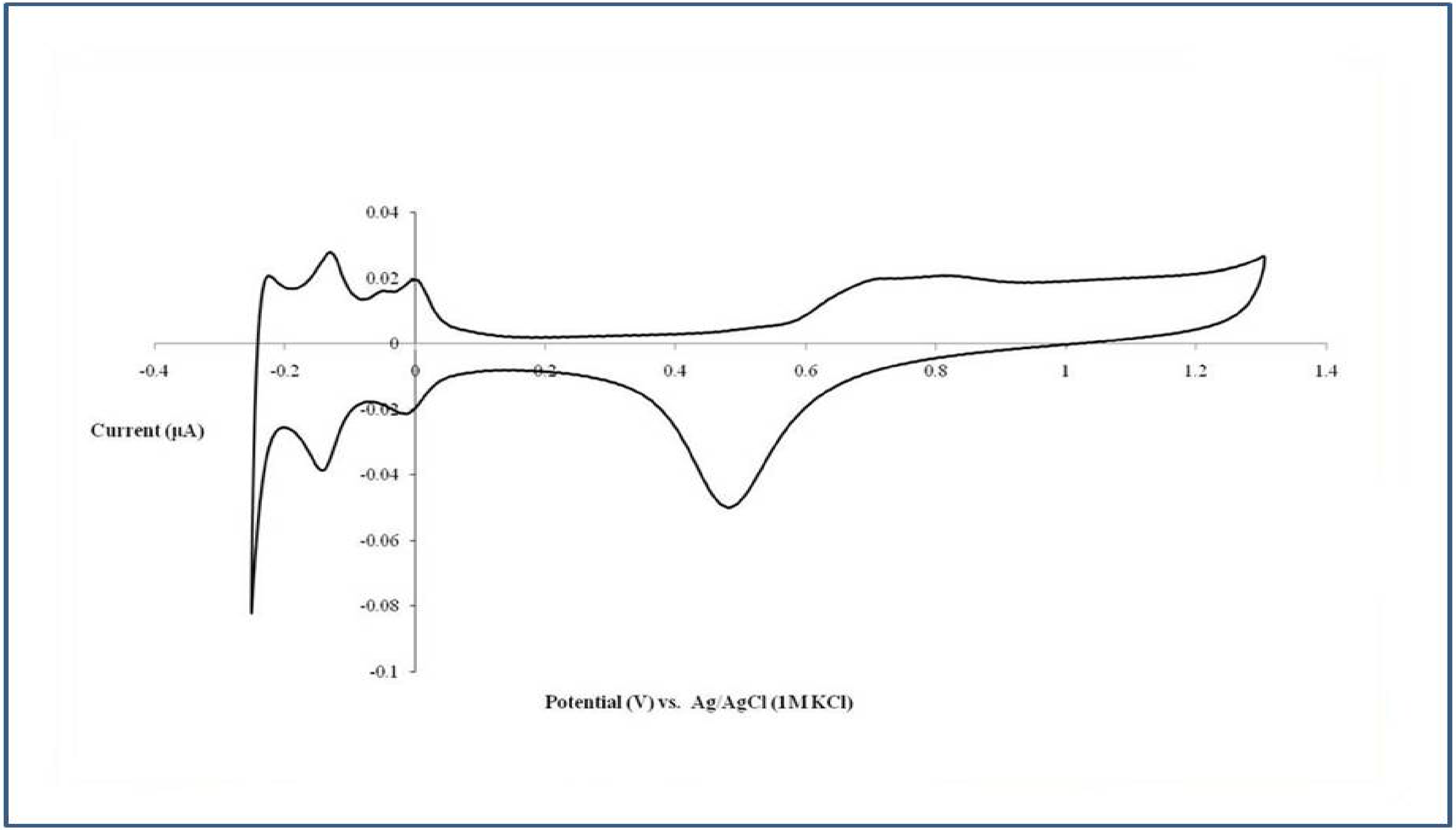
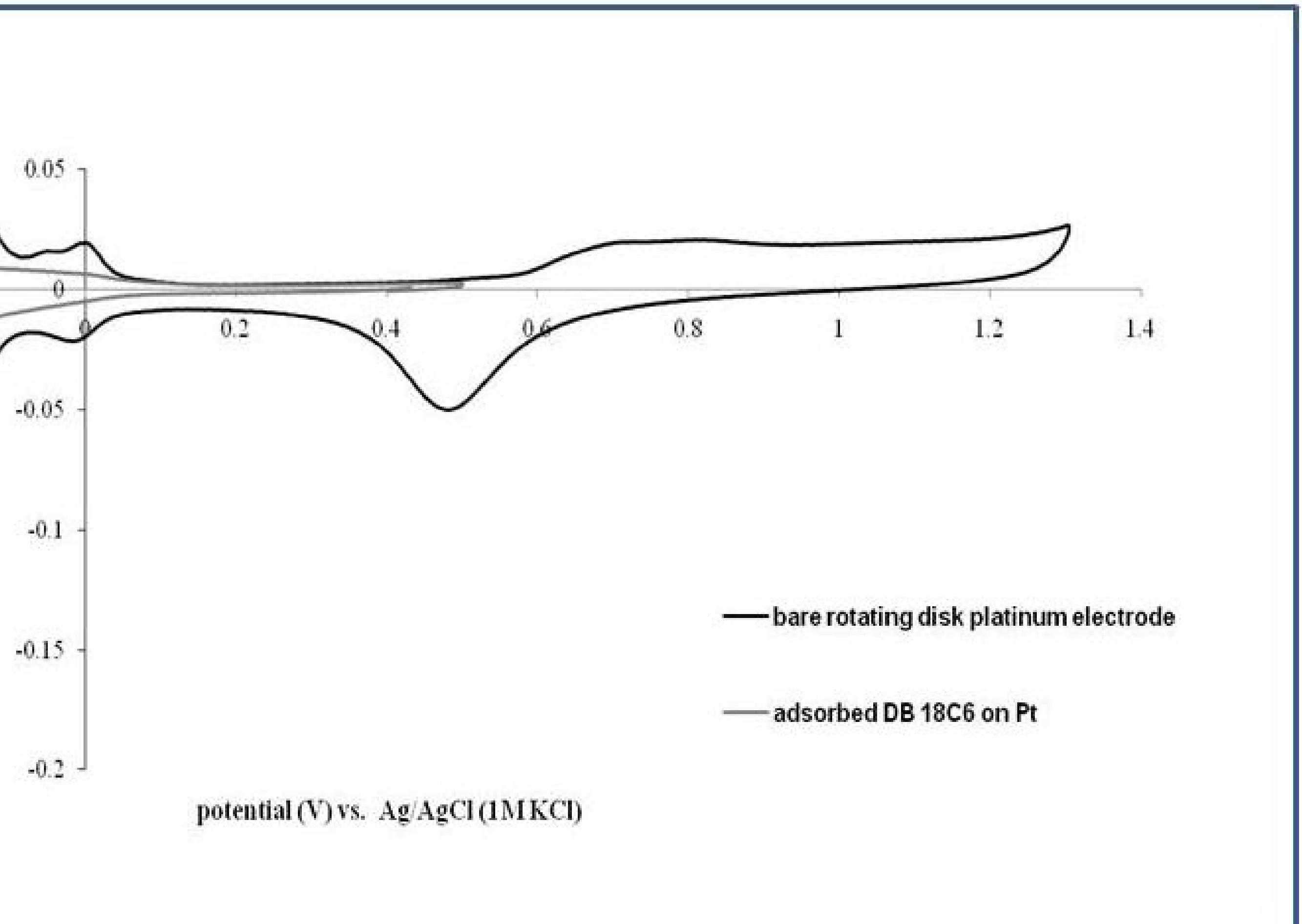


Figure 3.2 Cyclic voltammogram of a polycrystalline rotating disk platinum electrode (RDE) in 0.5 M H_2SO_4 at scan rate 50mV/s

3.2 Adsorption of DB 18C6 onto polycrystalline stationary platinum and rotating disk platinum electrodes

Many substances were spontaneously adsorbed on a substrate surface from solution, forming a monolayer on the electrode surface; this is due to the fact that the substrate environment is energetically more favorable than that in solution (Bard, *et al.*, 2001).

Figure 3.3 shows that E-i potentiodynamic curve for a platinum electrode pretreated with DB18C6 at open circuit conditions. It can be observed in this Figure, that DB18C6 adsorb chemically intact in a limited potential region between 500 and -250 mV. The DB18C6 adsorbed on platinum is extremely stable; it is not desorbed by rinsing the electrode with water or 0.5 M H_2SO_4 solution. Under ambient conditions, crown ether can be removed from the surface by excessive cyclization of the electrode potential between hydrogen and oxygen evolution limits. Cyclization of the electrode in the hydrogen and double-layer region is stable as far as the potential is not scanned in the oxidation region.


0.05
0
-0.05
-0.1
-0.15
-0.2
0.2
0.4
0.6
0.8
1
1.2
1.4
bare rotating disk platinum electrode
adsorbed DB 18C6 on Pt
potential (V) vs. Ag/AgCl (1M KCl)

These figures showed the reduced charge for hydrogen adsorption and desorption. The suppression of the surface area available for hydrogen adsorption on platinum surface indicates that DB18C6 was adsorbed on its surface and it is partially covered with it. Adsorption of DB18C6 does not totally inhibit hydrogen adsorption on the platinum electrode. The difference between the charges for hydrogen desorption in the absence and in the presence of DB18C6 represent the area of the electrode that is covered with DB18C6.

Adsorption of the crown ethers was carried out at open circuit in 1×10^{-3} M crown ether solution in 0.5 M H_2SO_4. The Polycrystalline platinum electrode real surface area was 0.536 cm^2 and for RDE was 0.203 cm^2 real surface area as determined from the voltammograms. The coverage of adsorbed DB18C6 on polycrystalline stationary platinum and RD Pt electrodes, was calculated as 0.711, 0.680 respectively.

The coverage of DB18C6 on platinum surface is relatively high and indicates that the surface is highly loaded with DB18C6 .This fact reflects the stronger interaction of the π-electrons of the benzene groups with the platinum surface, leading to higher coverage (Bußar et al., 2005).

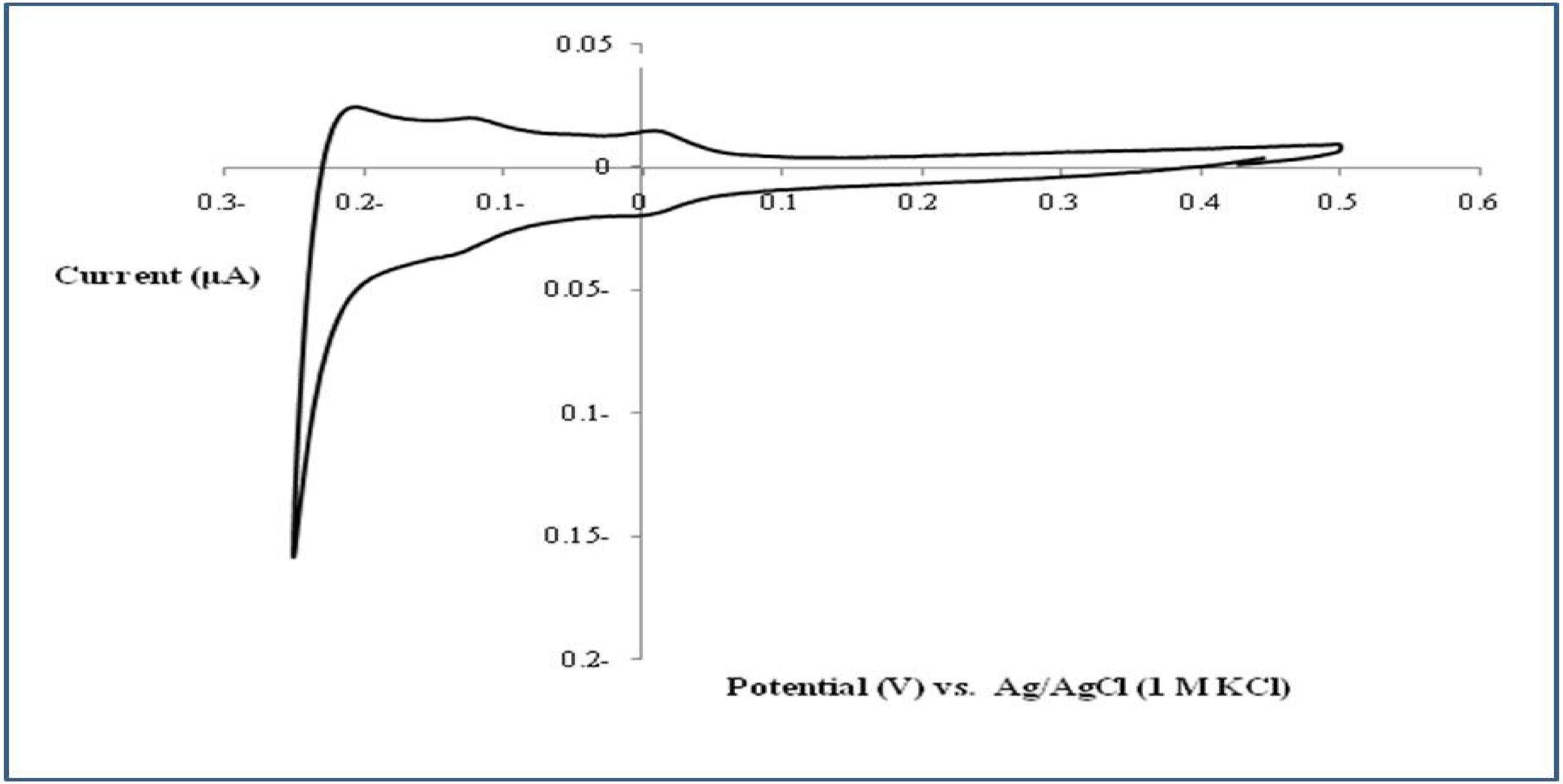


Figure 3.3 Cyclic voltammogram for a polycrystalline platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in 0.5 M H_2SO_4, negative going scan; at 50mV/s

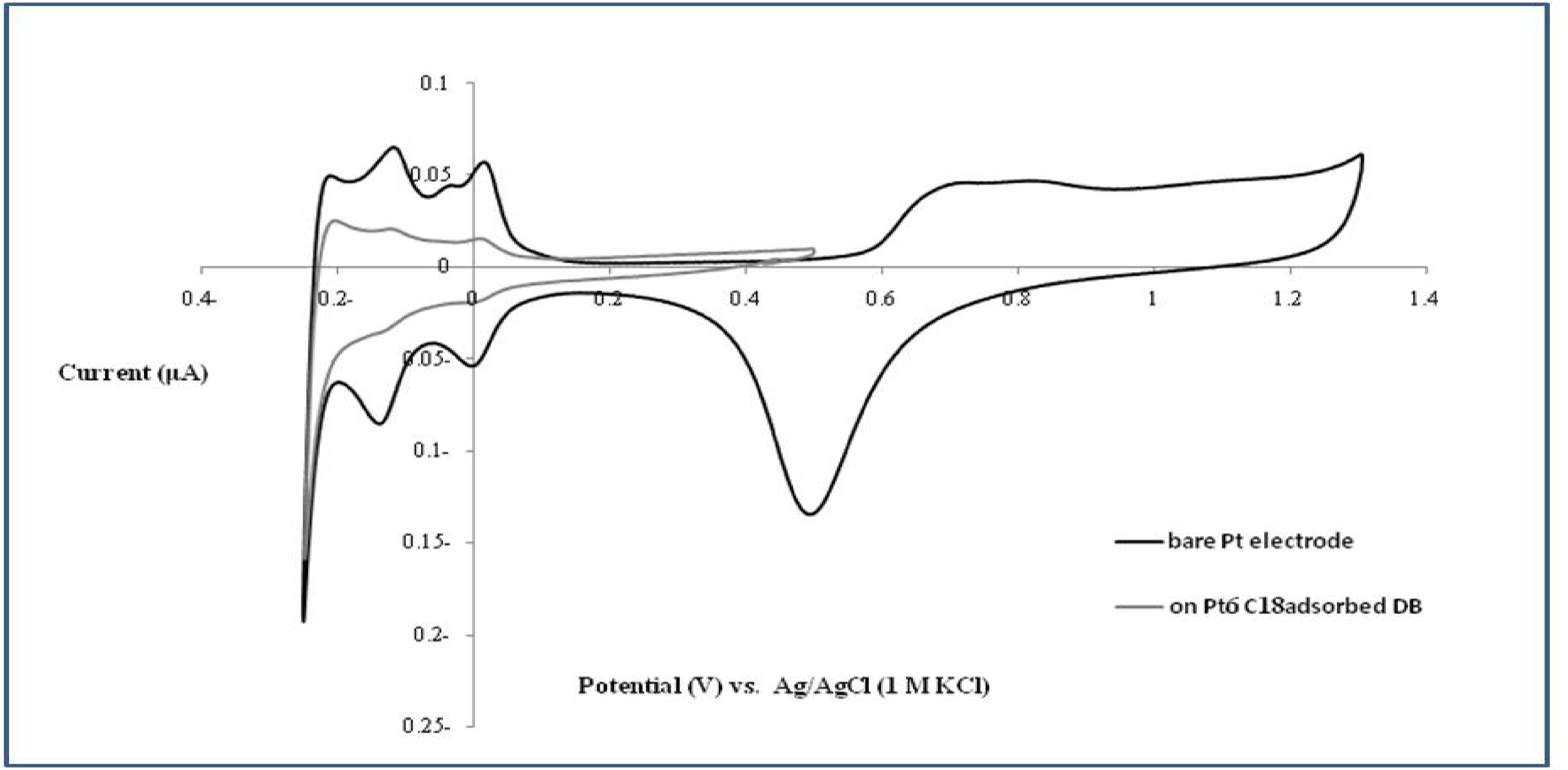


Figure 3.4 Cyclic voltammogram of a polycrystalline stationary platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in 0.5 M H_2SO_4 at scan rate 50mV/s

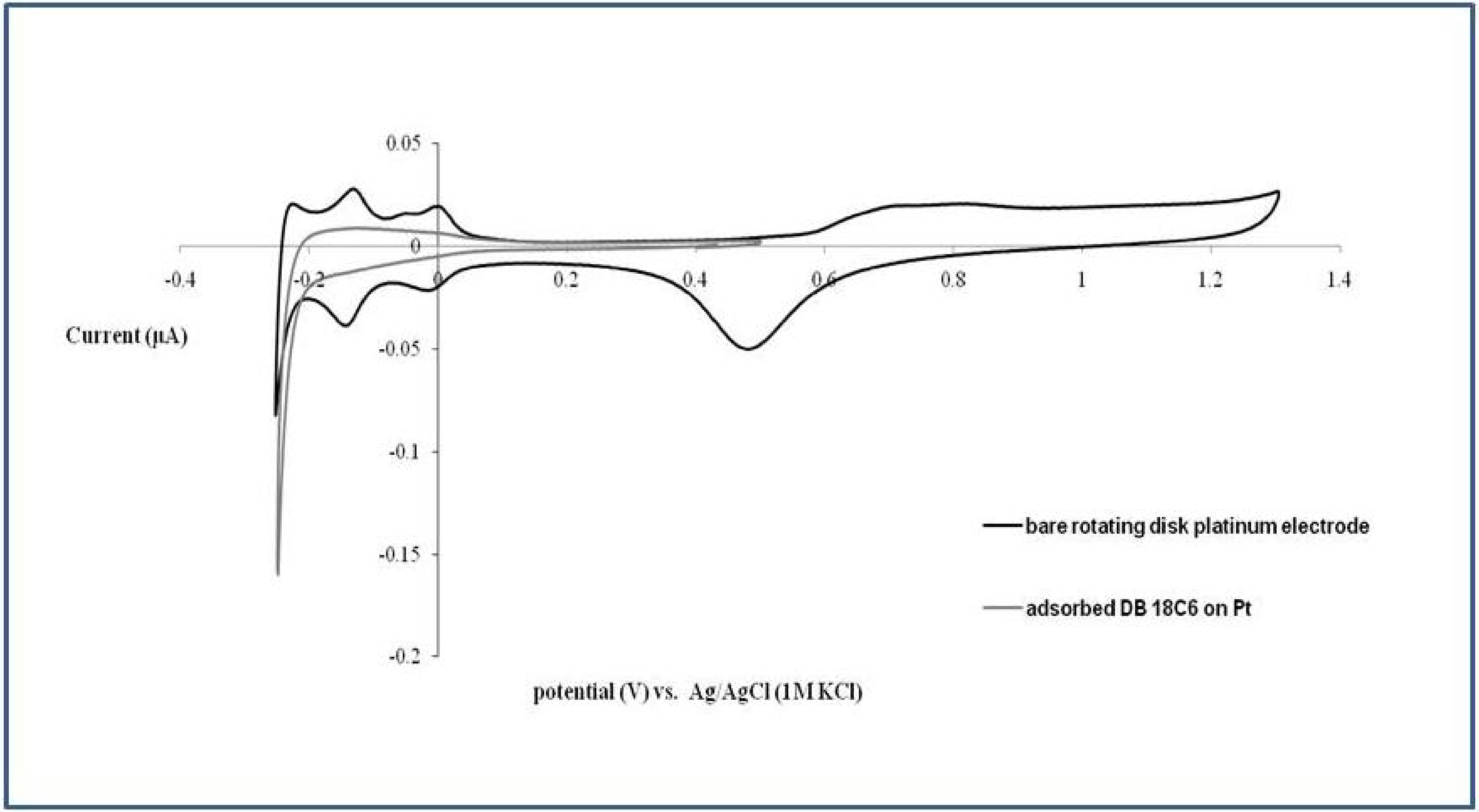


Figure 3.5 Cyclic voltammogram of a polycrystalline rotating disk platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in 0.5 M H_2SO_4 at scan rate 50mV/s

3.3 Electroanalysis of silver and copper ions by the modified electrodes

3.3.1 Polycrystalline stationary platinum electrode

Figure 3.6 shows a representative cyclic voltammograms for DB 18C6-coated Platinum electrode in 0.5 M H_2SO_4 with different concentrations of silver solutions. This Figure shows distinct peaks for oxidation and reduction of silver ions superimposed on negligible background. The voltammogram shows cathodic peaks for reduction (or deposition) of Ag^+ centered at about 0.33 V and an anodic peaks centered around 0.42 V. The little differences in peak potentials for different silver concentrations are expected, due to the different electrochemical reactions. The relationship between the anodic peak current (i_p) and the concentrations of silver in the bulk is linear with a regression coefficient of 0.99 (Figure 3.8). This result indicates that DB 18C6- coated platinum electrode can be used for analysis of monovalent cations which be deposited on its surface.

Applicability of the DB 18C6-coated platinum electrode for the analysis of divalent cations was demonstrated by the analysis of copper (II) ions. Figure 3.7 shows a cyclic voltammograms for DB 18C6- coated Platinum electrode in 0.5 M H_2SO_4 with different concentrations of copper solutions. The voltammogram shows two distinct, fairly resolved anodic peaks, the first peak is centered at about 0.1 V while the second is centered at -0.07 V, based on peak sharpness criterion, the first anodic peak was chosen. These two peaks, most likely, represent the oxidation of Cu to Cu^+ followed by oxidation of Cu^+ to Cu^{2+}.

Peak currents were measured and plotted against the concentrations of Cu^{2+} in the solution (Figure 3.9). Statistical analysis of the data showed that the relationship between i_p and the concentrations of Cu^{2+} are linear with a regression coefficient of 0.9917.

Also, a mixture of Ag^{+} and Cu^{2+} with equal concentration (1×10^{-3} for each one) was studied. Figure 3.10 shows a peak for Ag^{+} at about 0.37 V and two peaks for Cu^{2+} one at -0.05 V and the other at about 0.08 V; these peaks are well resolved from the silver peak. From this result it can be concluded that this modified electrode can easily differentiate between silver and copper ions.

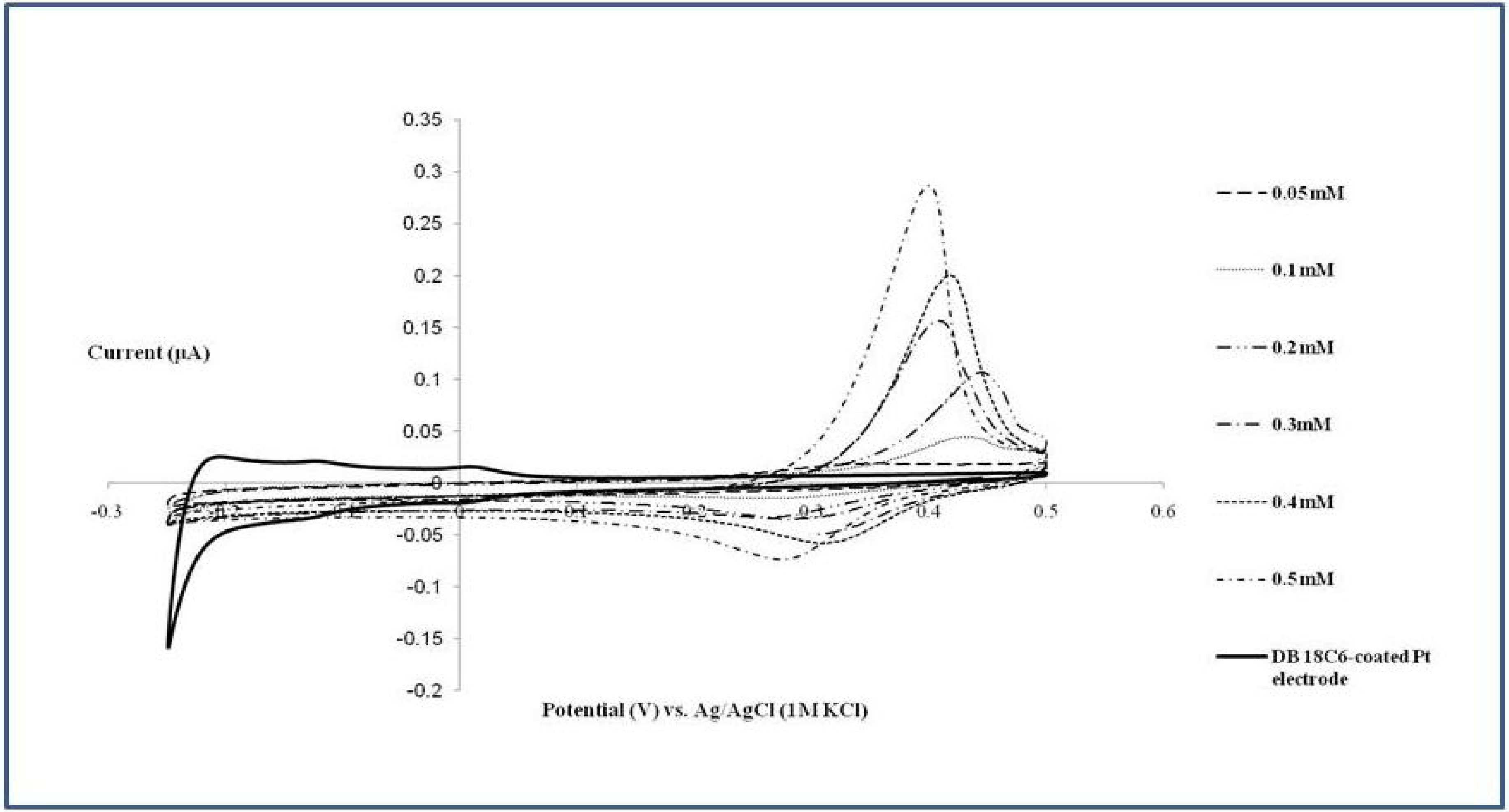


Figure 3.6 Cyclic voltammograms of a polycrystalline platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in different concentrations of silver in 0.5 M H_2SO_4 at 50mV/s

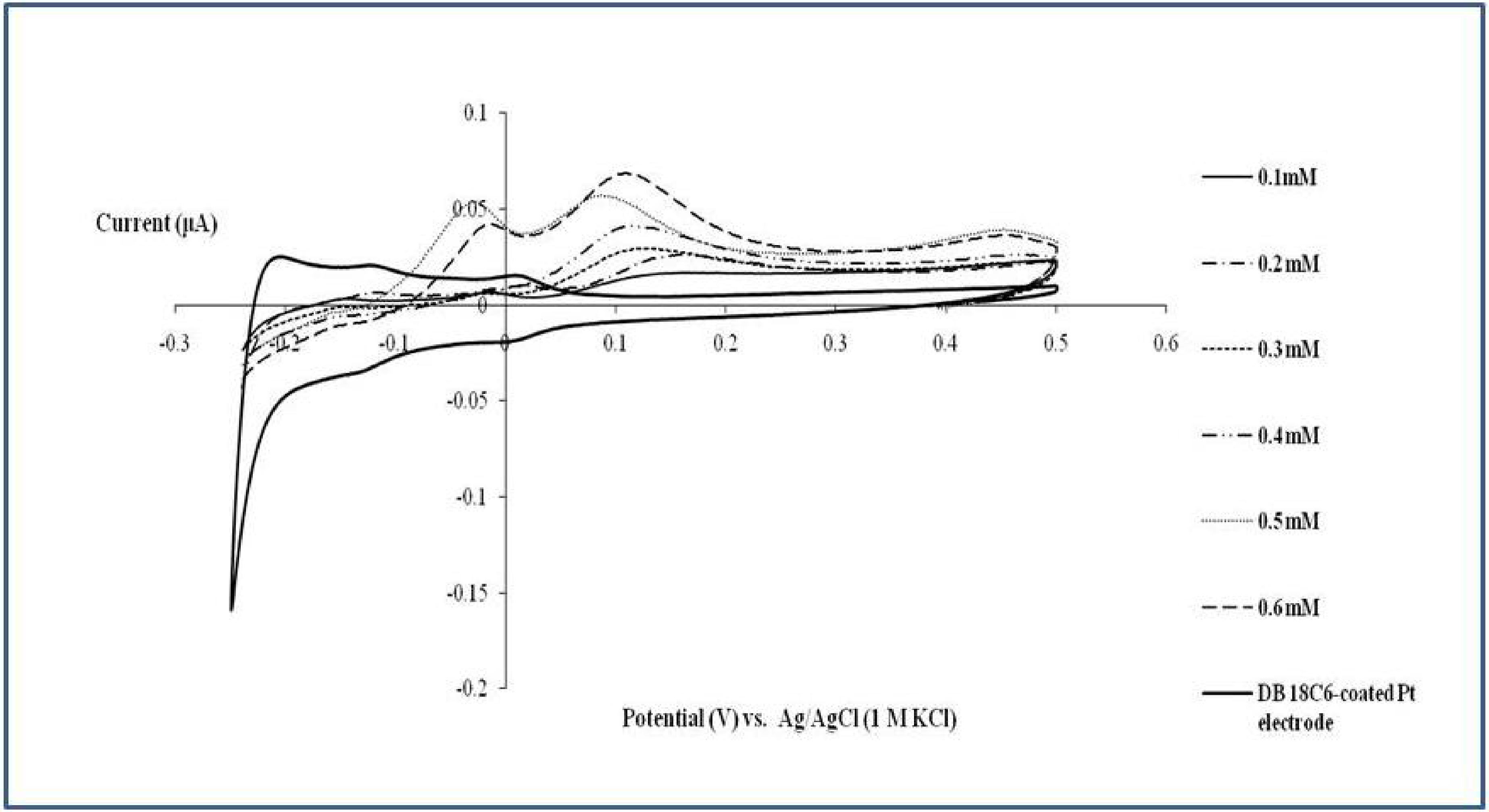


Figure 3.7 Cyclic voltammograms of a polycrystalline platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in different concentrations of copper in 0.5 M H_2SO_4 at 50mV/s

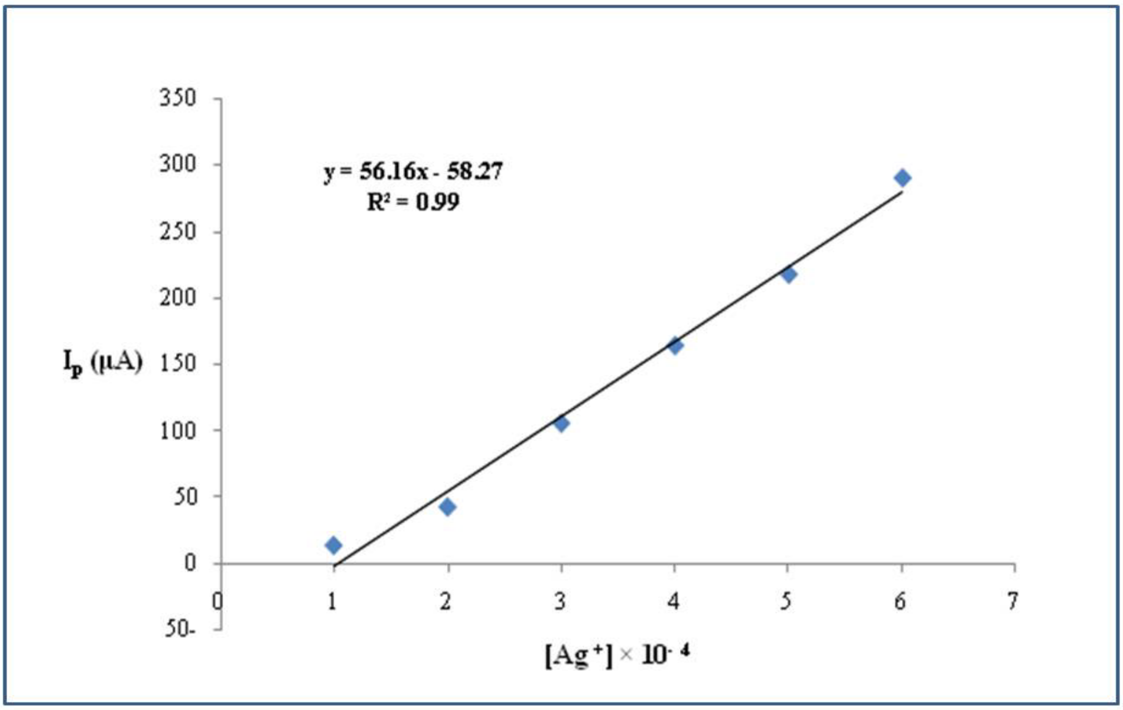


Figure 3.8 A plot of peak current (i_p) for silver ions extracted from the (E-i) curve at DB-18-C6 modified platinum electrode in 0.5 M H_2SO_4 vs. the concentration of Ag^+ in the solution (scan rate =50 mV/s)

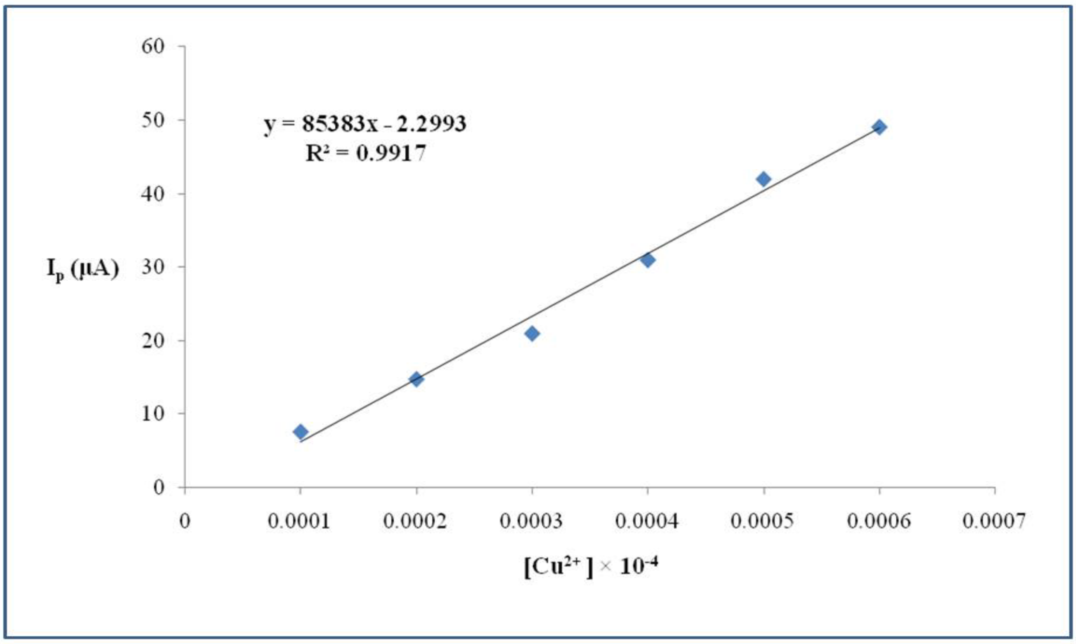


Figure 3.9 a plot of peak current (i_p) for copper ions extracted from the (E-i) curve at DB-18-C6 modified platinum electrode in 0.5 M H_2SO_4 vs. the concentration of Cu^{2+} in the solution (scan rate =50 mV/s)

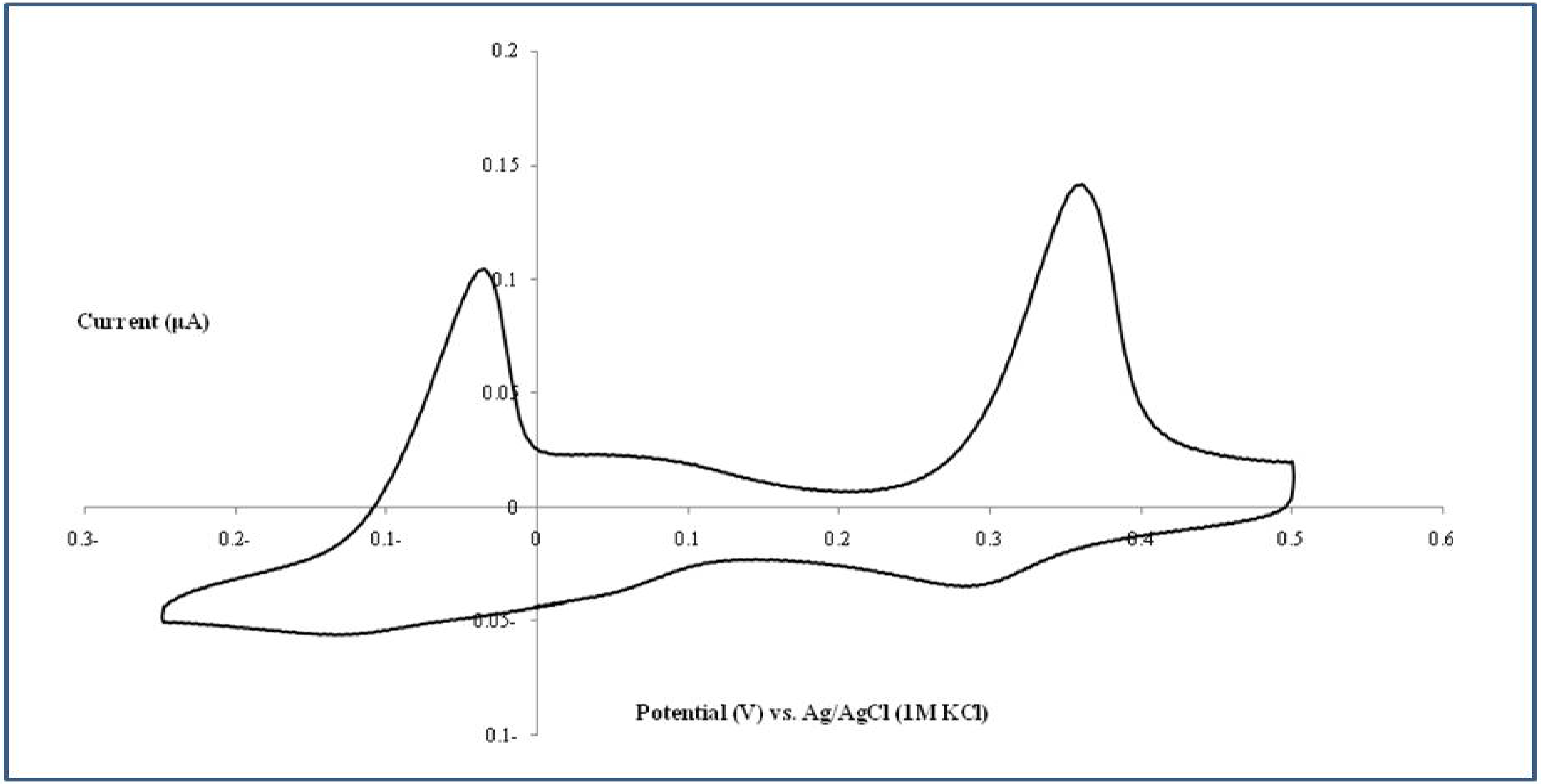


Figure 3.10 Cyclic voltammogram of a polycrystalline platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in concentrations of copper and silver (1× 10^{-3} M for each one) in 0.5 M H_2SO_4 at 50mV/s

3.3.2 Polycrystalline rotating disk platinum electrode

As it was mentioned before, there are several electrode configurations that give rise to steady-state measurements. Most common examples are the rotating (ring)-disk electrode.

Applicability of the DB 18C6-coated rotating disk platinum electrode in the analysis of ions was verified by electroanalysis of Ag^{+} and Cu^{2+} ions at 1000 rpm. This cylinder, with its end immersed in solution, is rotated about its vertical central axis at a speed low enough to avoid turbulence flow (typically 1000 revolutions per minute (rpm)) (De Strycker et al., 2001).

Figure 3.11 shows the E-i curve for DB 18C6-coated platinum electrode traced in 0.5 M H_2SO_4 solution containing variable small concentrations of Ag^{+}. Anodic peak currents (which centered at about 0.45 V) were extracted from the voltammogram and plotted against the concentrations of Ag^{+} (Figure 3.13). Analysis of the data indicates that the relationship between i_p and the concentration of Ag^{+} is linear with a regression coefficient of 0.9942.

Figure 3.12 shows the E-i curve for DB 18C6-coated platinum electrode traced in 0.5 M H_2SO_4 solution containing variable small concentrations of Cu^{2+} with the anodic peak currents centered at about 0.15 V.

Figure 3.14 shows a good linear relationship between i_p and the concentrations of Cu^{2+} with a regression coefficient of 0.9947.

As it shown here a smaller concentrations could be analyzed by the rotating disk electrode, in the range of 10^{-6} M that could not be analyzed by the stationary electrode. The reason is due to the fact that is the electroactive species transfer in the stationary electrode by diffusion alone, but in RDE (hydrodynamic system), they transfer by diffusion and convection (hydrodynamic transfer), also the steady-state has been reached readily, so this lead to high sensitivity.

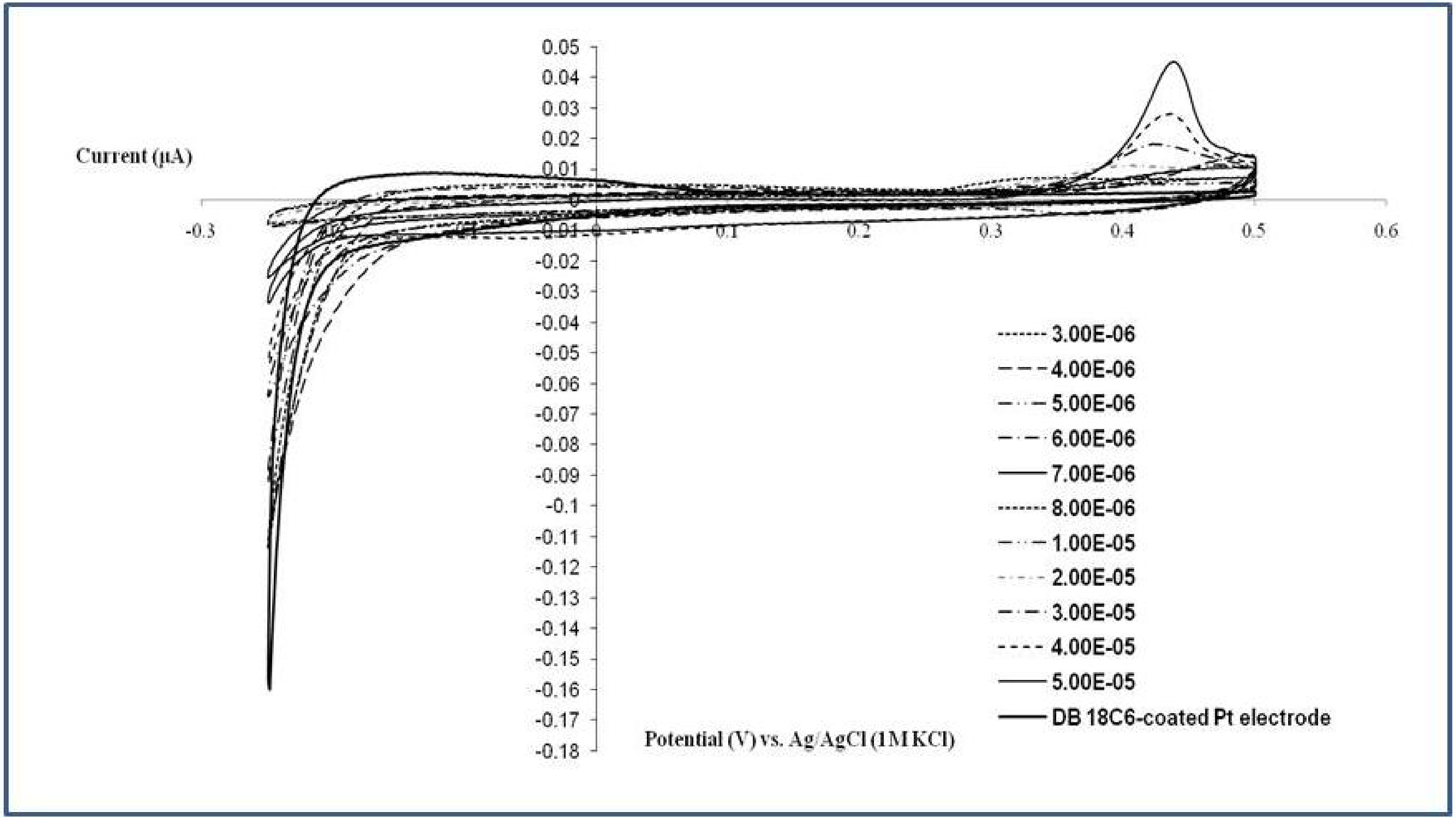


Figure 3.11 Cyclic voltammograms of a polycrystalline rotating disk platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in different concentrations of silver in 0.5 M H_2SO_4 at 50mV/s

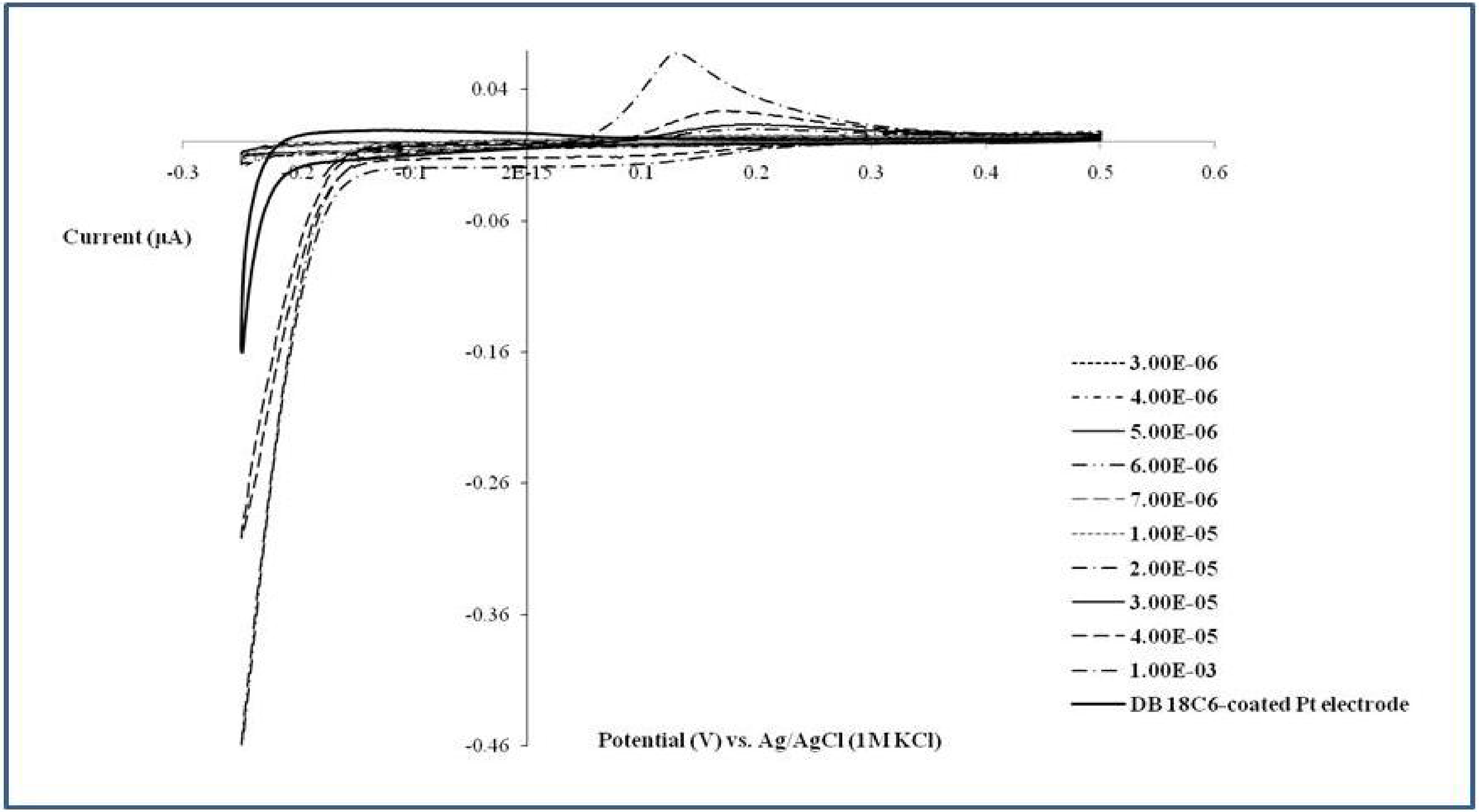


Figure 3.12 Cyclic voltammograms of a polycrystalline rotating disk platinum electrode pretreated at open circuit for 10 min with saturated Dibenzo-18-crown-6 in different concentrations of copper in 0.5 M H_2SO_4 at 50mV/s

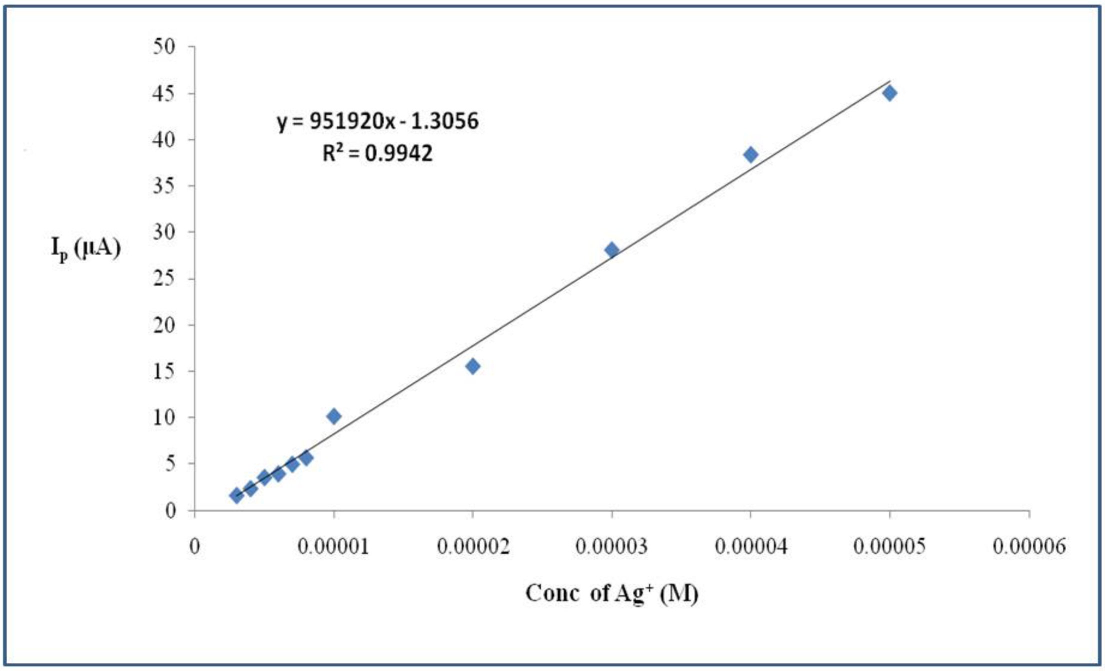


Figure 3.13 a plot of peak current (i_p) for silver ions extracted from the (E-i) curve at DB-18-C6 modified rotating disk platinum electrode in 0.5 M H_2SO_4 vs. the concentration of Ag^+ in the solution (scan rate =50 mV/s)

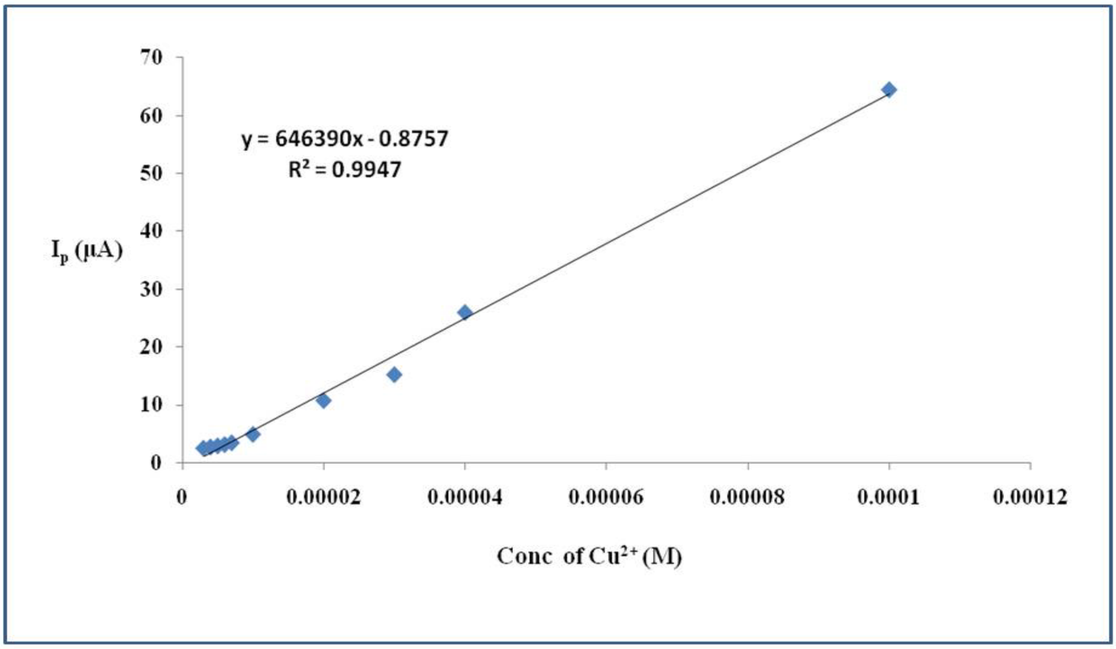


Figure 3.14 a plot of peak current (i_p) for copper ions extracted from the (E-i) curve at DB-18-C6 modified rotating disk platinum electrode in 0.5 M H_2SO_4 vs. the concentration of Cu^{2+} in the solution (scan rate =50 mV/s)

3.3.3 Variation of i_p with $\omega^{1/2}$ in rotating disk electrode

A rotating disk electrode reaches a steady-state through a combination of convention and diffusion of electro-reactant to the electrode surface. This steady-state gives rise to regions in the voltammogram where the current is independent of the potential, defined as limiting current plateau. The limiting current corresponding to this plateau obeys the Levich-equation

$$I_l = 0.620\ nFA(d/\eta)^{1/6} D_i^{2/3} \omega^{1/2} c_i,$$

I_l = limiting anodic or cathodic current (A)

n= number of electrons exchanged in the reaction

F= Faraday constant (96485 C mol^{-1})

A= electrode surface area (m^2)

d= density (Kg m^{-3})

η= viscosity (Pa)

D_i = diffusion coefficient ($m^2\ s^{-1}$)

ω = rotation rate of the electrode (rad s^{-1})

ci= concentration of the reacting substance in solution (mol m^{-3})

At a steady state no changes are occurring with time in the proprieties (concentrations, flux, densities, etc.) of interest, despite there being transport between different regions of the system. Solvent molecules at the surface region rotate with the same speed as the electrode (De Strycker et al., 2001).

In these solutions; 1×10^{-5} M Ag^{+} and 1×10^{-5} M Cu^{2+}, it took from 15-20 minutes to reach a steady-state current at a rotating disk electrode. This time depends on the viscosity of the solution and the diffusion coefficient of the reacting species.

Figure 3.15 and Figure 3.17 show that as the rpm increases, Ag^{+} stripping peak increases, at a rotation rate from 100- 1000 rpm, but after 1000 rpm up to 1500, the peak current height remains almost at the same value, and no great difference in height is shown, which can be explained on basis of kinetic limitations.

Figure 3.16 and Figure 3.18 showed that as the rotation rate increases, the peak of the Cu^{2+} increases too and that is from 100- 900 rpm, and then it's become constant most probably due to kinetic limitations.

A deviation of a plot of i_p vs. $\omega^{1/2}$ from straight line which occurred after 1500 rpm as in figure 3.15 for Ag^{+} solution and after 900 rpm as in figure 3.16 for Cu^{2+} solution suggests that a kinetic limitation is involved in the electron- transfer step (Bard and Faulkner, 2001).

Also the loose of linearity occurred after a certain number of (rpm) as mentioned above is due to the fact that; a rotating disk electrode has no growing diffusion layer after the steady-state has been reached. This means that the concentration gradient remains the same during the period that steady-state is obtained and thus the current must become constant (De Strycker et al., 2001).

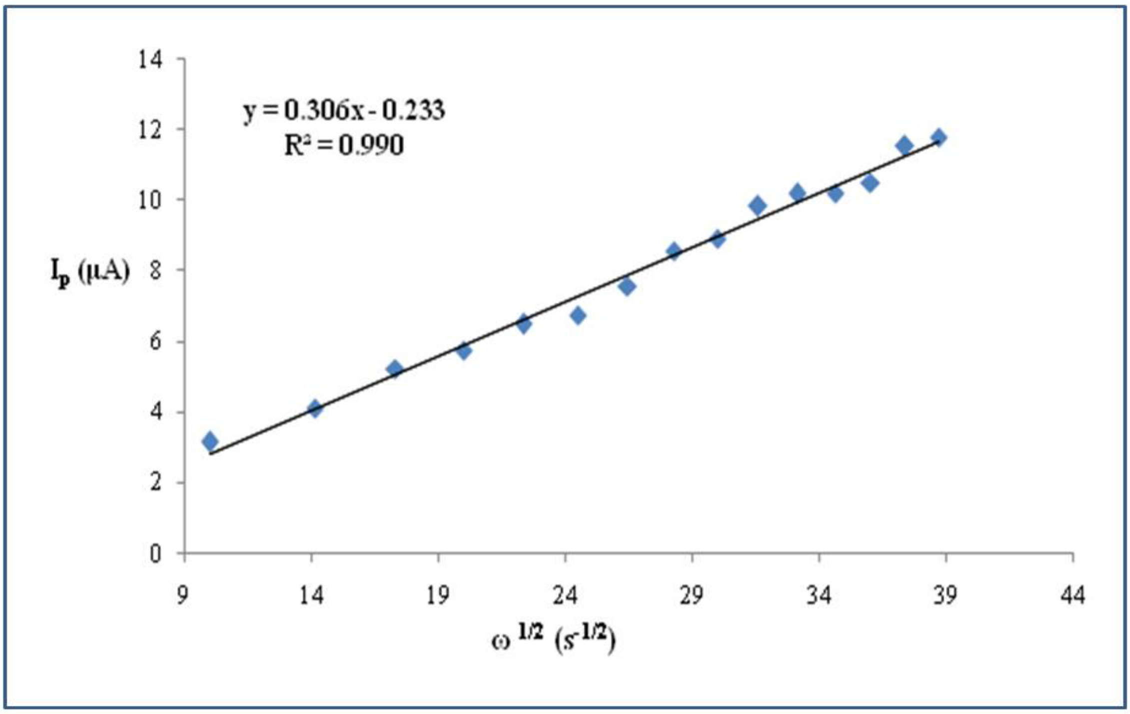


Figure 3.15 a plot of (i_p) for silver ions extracted from the (E-i) curve at DB-18-C6 modified rotating disk platinum electrode in 0.5 M H_2SO_4 vs. the $\omega^{1/2}$ (scan rate =50 mV/s)

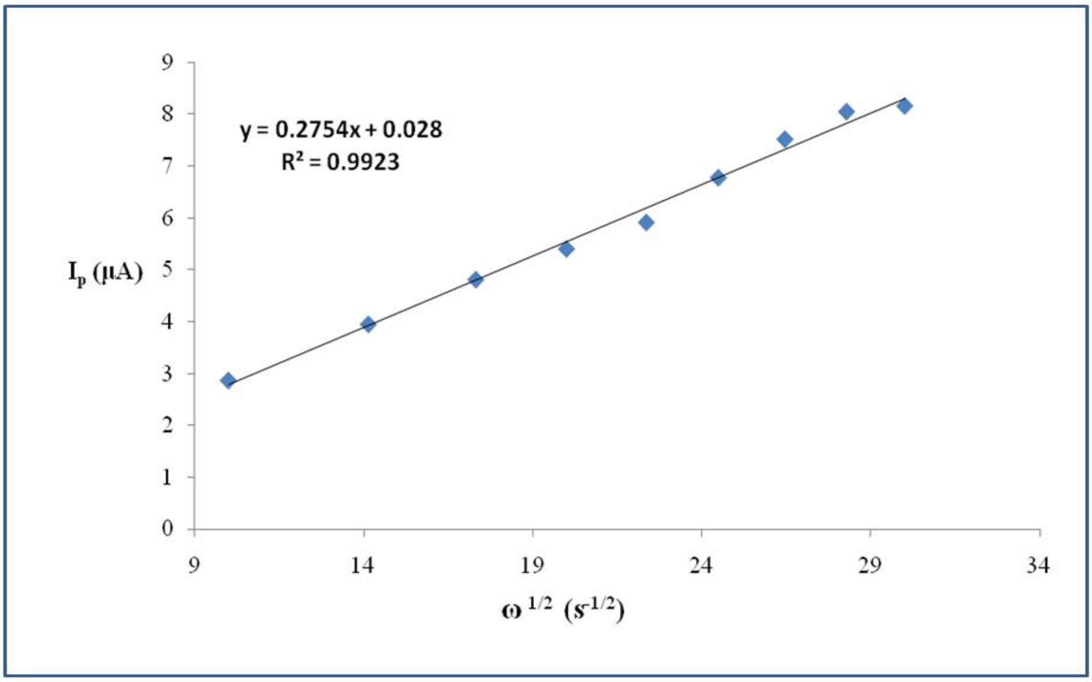


Figure 3.16 a plot of (i_p) for copper ions extracted from the (E-i) curve at DB-18-C6 modified rotating disk platinum electrode in 0.5 M H_2SO_4 vs. the $\omega^{1/2}$ (scan rate =50 mV/s)

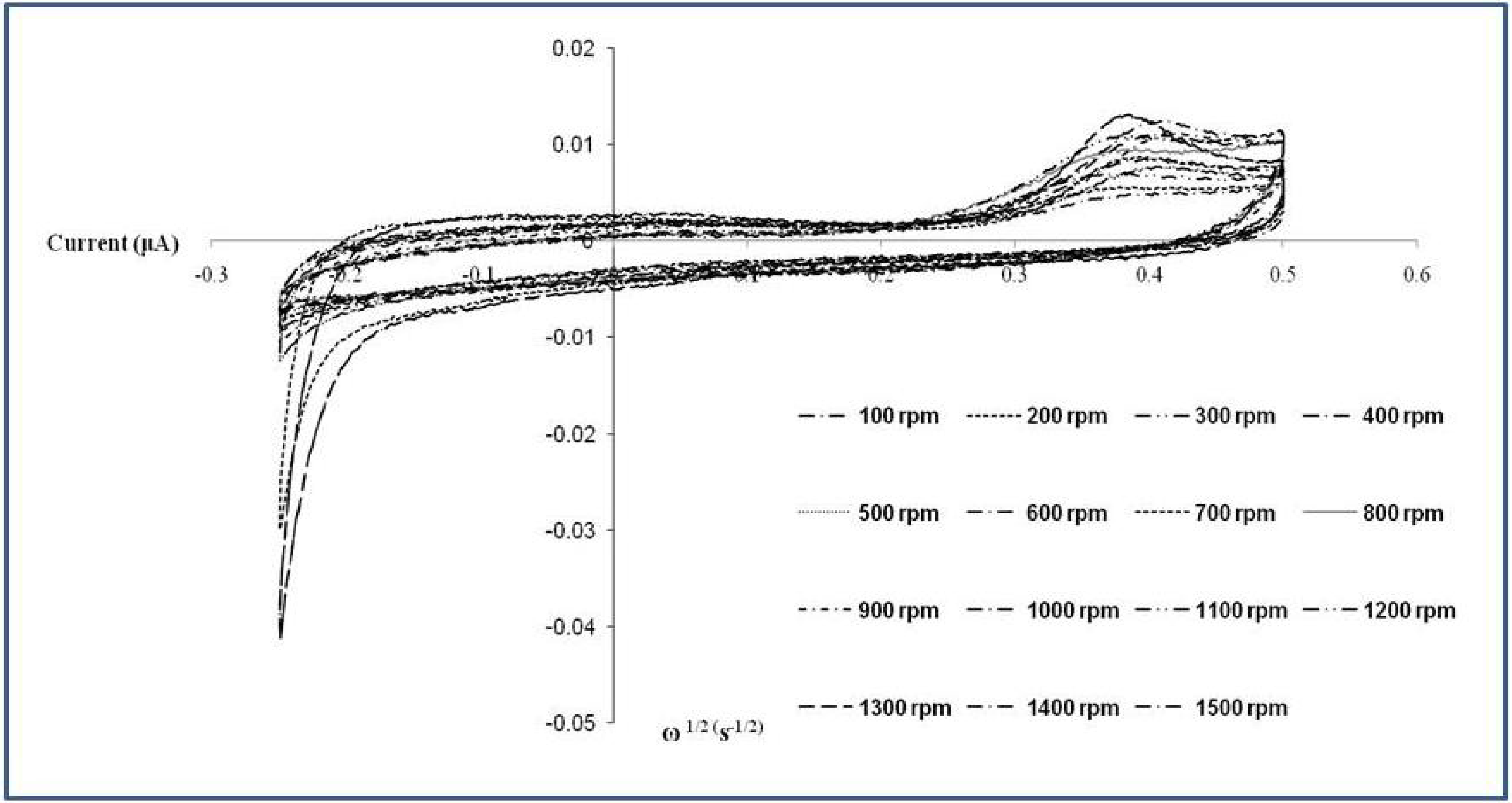


Figure 3.17 cyclic voltammograms of peak currents (i_p) for 1×10^{-5} M silver ions extracted from the (E-i) curve at DB-18-C6 modified rotating disk platinum electrode in 0.5 M H_2SO_4 vs. the angular velocity ($\omega^{1/2}$) at scan rate 50 mV/s

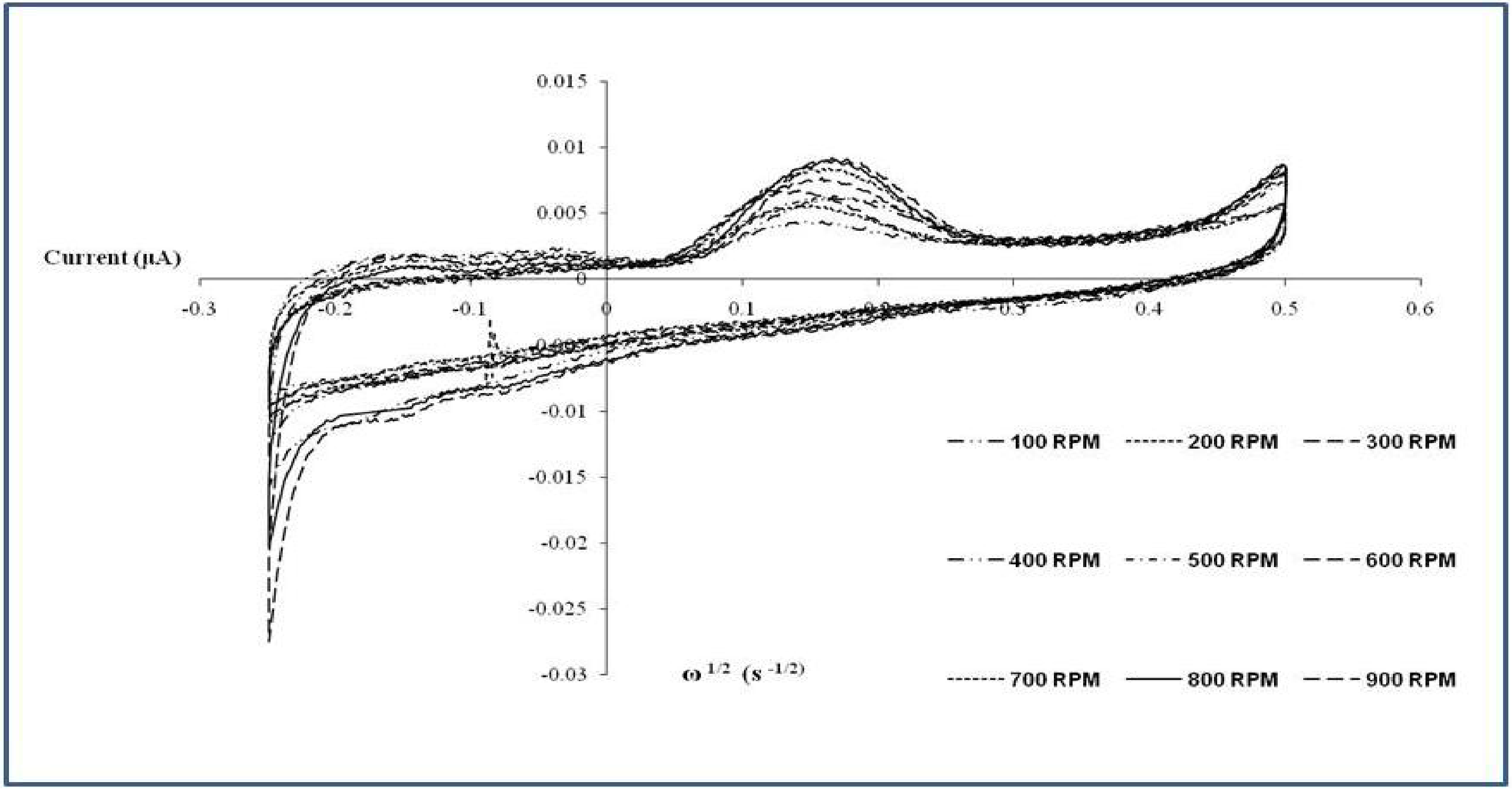


Figure 3.18 cyclic voltammograms of peak currents (i_p) for 1×10^{-5} M copper ions extracted from the (E-i) curve at DB-18-C6 modified rotating disk platinum electrode in 0.5 M H_2SO_4 vs. the angular velocity ($\omega^{1/2}$) at scan rate 50 mV/s

3.4 Anodic stripping analysis of Ag, Cu, Ni, and Cd solutions at a modified platinum wire electrode

Stripping voltammetric analysis has been as one of the most sensitive techniques and is widely used for the trace heavy metal analysis in various samples, because of its ability to preconcentrate the analytes on the electrode surface and to allow automatic (thus, low cost) in situ speciation measurements, with no or minimum sample change.

In trace analysis, mainly for heavy metal ions, anodic stripping voltammetry (ASV) is popular because of the low limit of determination – going down sub ppb concentrations, its accuracy and precision, as well as the low cost of instrumentation for this analytical technique (Kalvoda and Kopanica 1989).

In the present work, the DB 18C6-coated platinum electrode has been applied for stripping analysis of silver, copper, nickel and cadmium ions. Thus the contamination resistance of the DB 18C6-coated electrode and the excellent sensitivity of the stripping analysis technique have been combined for the analysis of these ions. The cyclic voltammetric responses of these ions were studied.

3.4.1 Anodic stripping analysis of silver ions at a modified polycrystalline platinum electrode

The voltammetric detection procedure consists of a preconcentration (accumulation), cathodic electrolysis (deposition) at a negative potential (-0.25 V), followed by stripping by scanning toward positive potential direction (0.5 V). Both cathodic electrolysis and stripping steps were done under quiescent conditions.

During preconcentration step, the electrode was immersed (at 1 cm from the solution surface) in a 25 ml of purged silver ions solution at open circuit for a specified period of time. After the stripping step, the electrode was removed, rinsed with triply distilled water and replaced in a purged 25 ml of 0.5 M H_2SO_4(as a supporting electrolyte solution). A negative going potential scan (0.5 to -0.25 V) was applied. After assurance that the electrode surface was clean and no metal was still left on the electrode surface; no peak of the metal will be detected in the cyclic voltammogram of the modified electrode. The same procedure was repeated with the time was increased 5 minutes for each new stripping experiment for every silver solution.

Figures 3.19 and 3.20 show the effect of preconcentration time on the voltammetric response using 5×10^{-7} M (0.054 ppm) Ag^+ solution. Peak currents are increased proportionally with time from 5 to 35 min and in parallel to each other at a potential of -0.0112 V. The observed current during the stripping step can be related to the amount of the metal in the solution.

The deposition step was performed by applying a negative potential (-0.25 V) which is sufficient for deposition of silver ions, followed by an anodic scan for stripping of silver.

Factors affecting the preconcentration of metal ions onto the electrode surface which in turn affect the voltammetric response in the detection step, include preconcentration time, pH of the solution, and concentration of the deposited ions (Lin ., et al 2004).

The anodic stripping peak currents increased upon changing the deposition time from 5 to 35 min with a regression coefficient of 0.9924 (Figure 3.23).

Figures 3.21 and 3.22 show a representative stripping voltammogram for a 5 x 10^{-9} M Ag^{+} (5.4 × 10^{-4} ppm) in 0.5 M H_2SO_4 solution. The voltammogram shows prominent sharp peaks centered at -0.0989 V. For a consistent set of experimental parameters, i.e., deposition time, deposition potential, surface area of the electrode, the position of silver stripping peak is independent of silver concentration in the test solution.

The relationship between stripping peak currents and silver deposition time was investigated from 5-45 min. A linear relationship with a regression coefficient of 0.9919 was obtained Figure 3.24.

This linear relationship between the deposition time and the stripping peak current indicates that the system was under mass transfer control (Hourani., 1999).

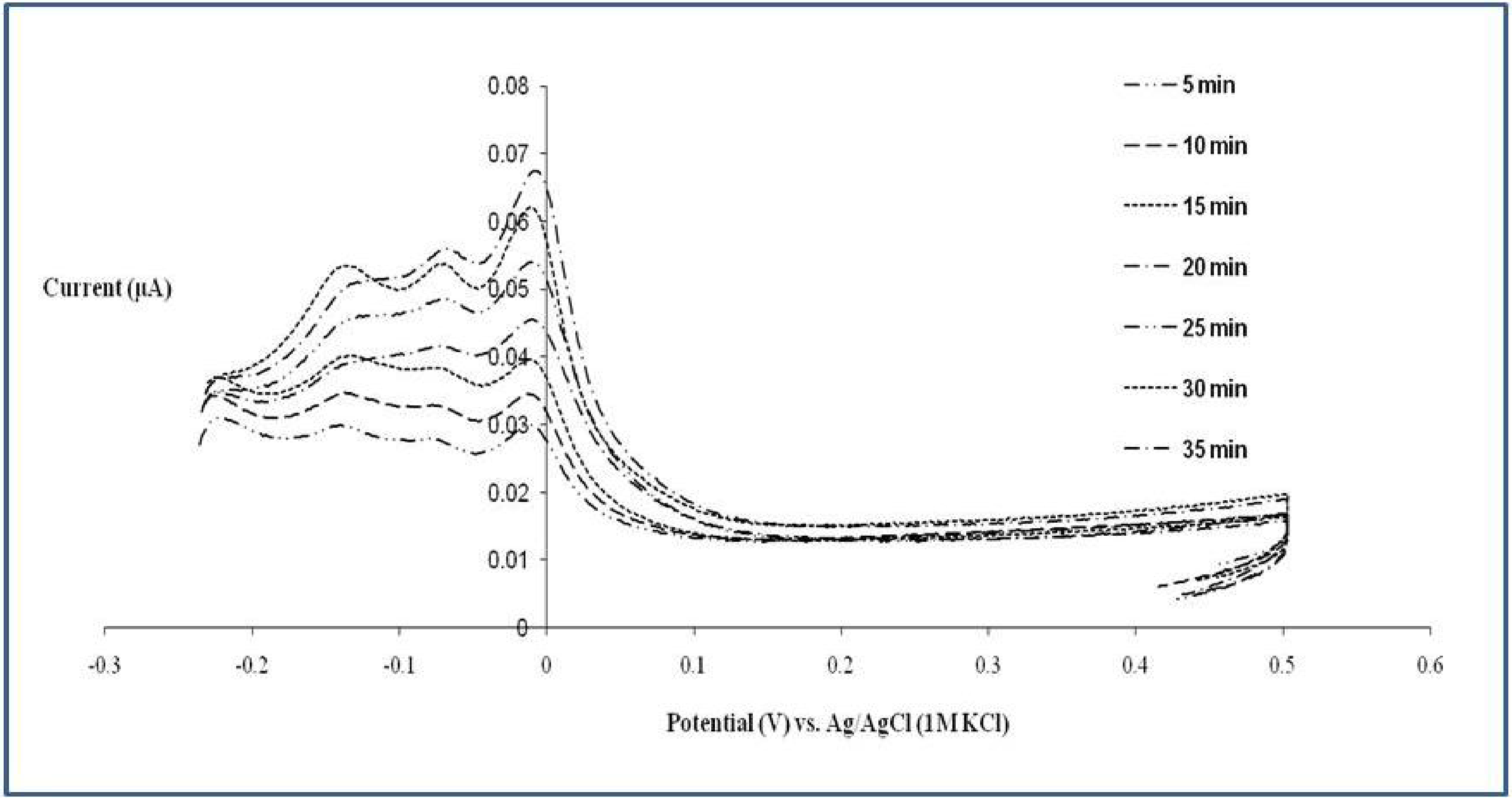


Figure 3.19 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-7} M Ag^{+} in 0.5 M H_2SO_4 at different deposition times

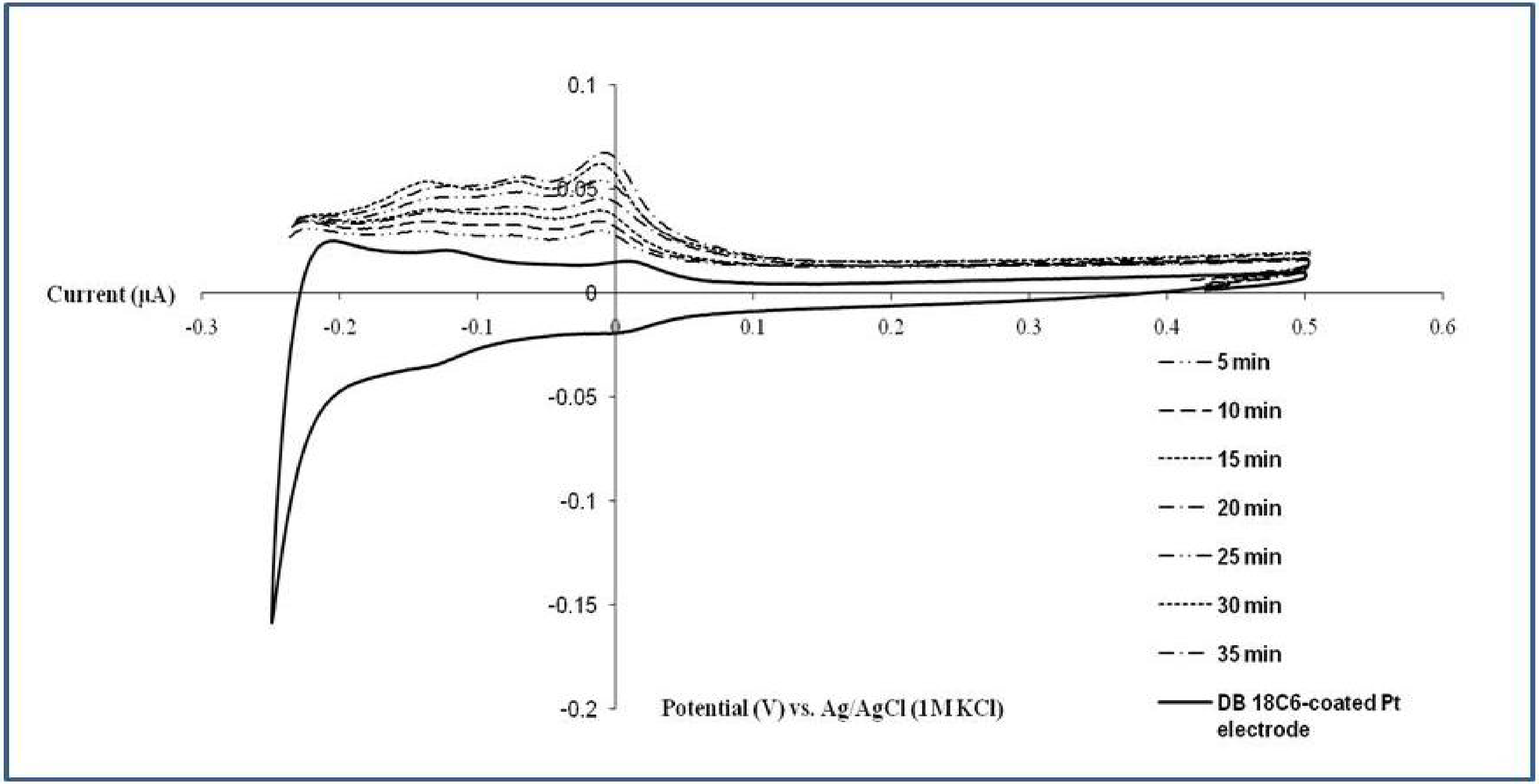


Figure 2.20 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-7} M Ag^{+} in 0.5 M H_2SO_4 at different deposition times (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

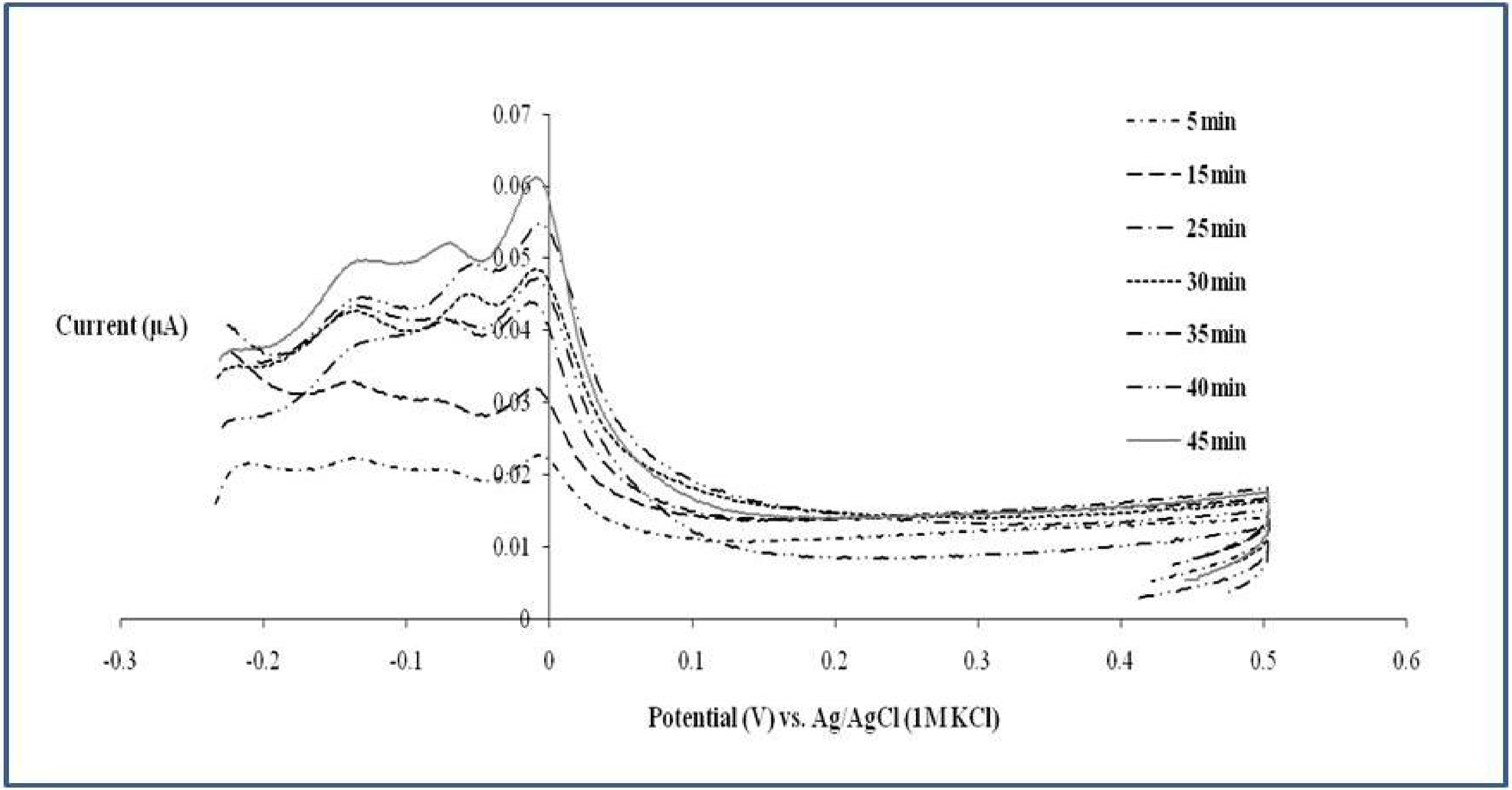


Figure 3.21 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-9} M Ag^{+} in 0.5 M H_2SO_4 at different deposition times

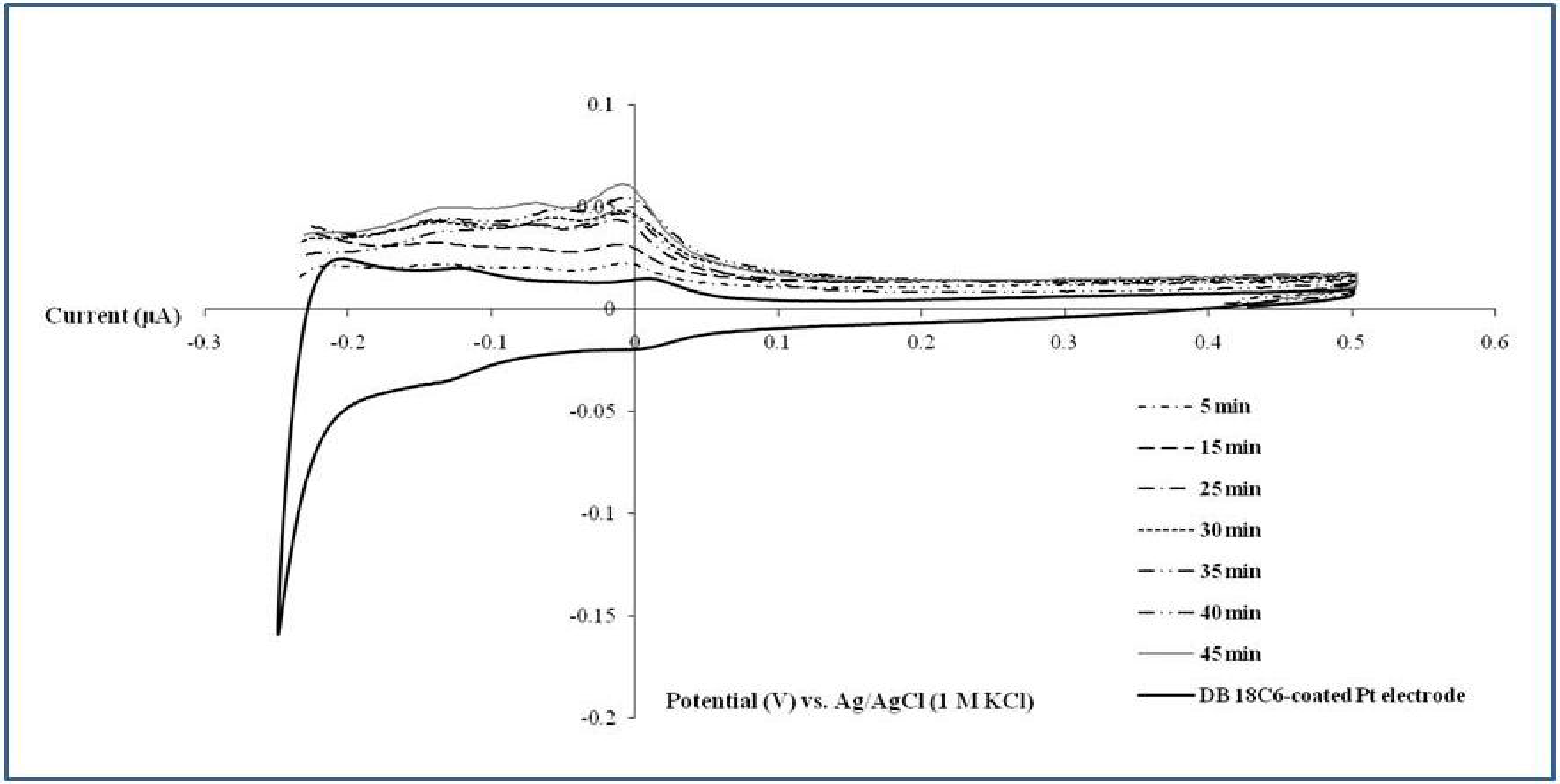


Figure 3.22 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-9} M Ag^+ in 0.5 M H_2SO_4 at different deposition times (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

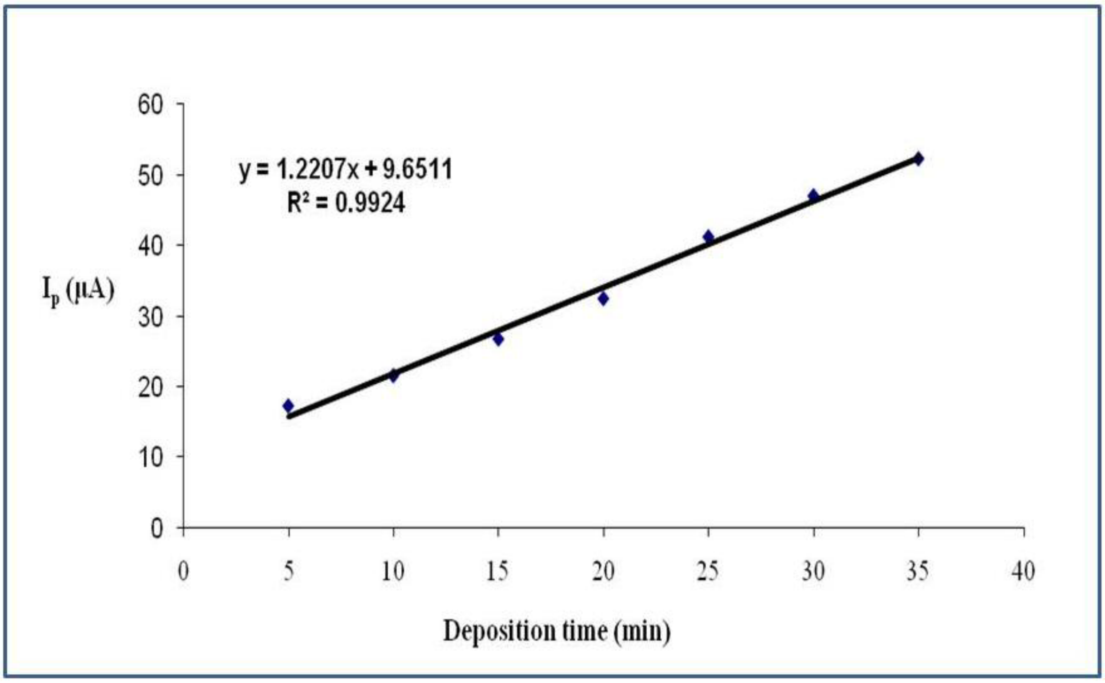


Figure 3.23 a plot of peak current (i_p) for silver-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing 5 × 10^{-7} M silver ions vs. the deposition time

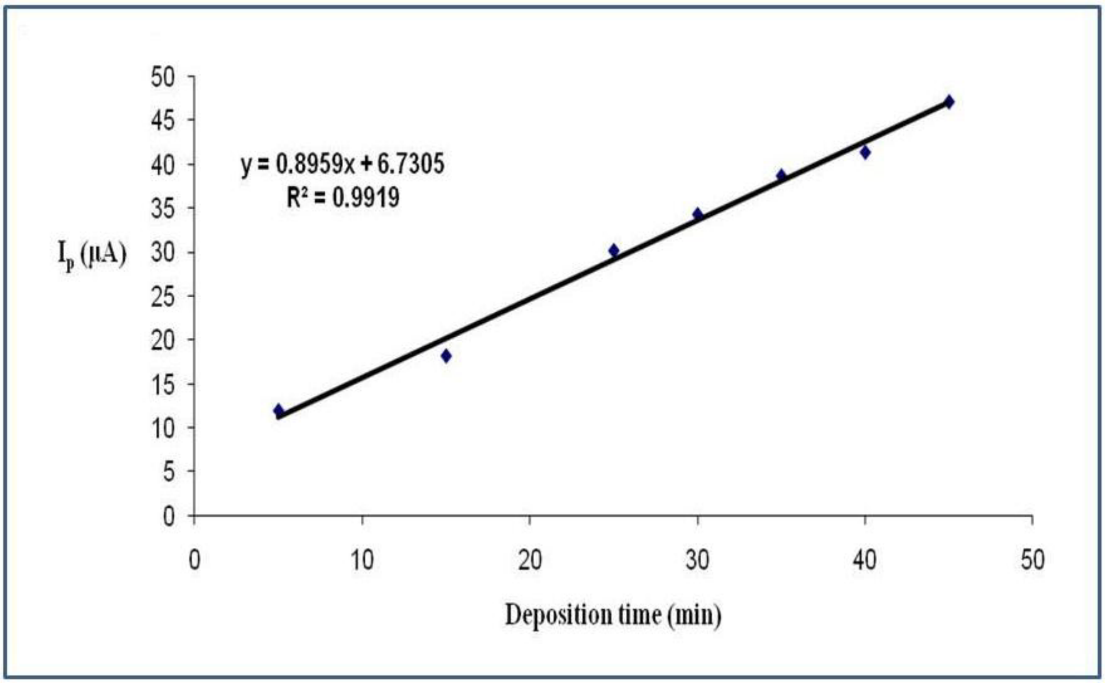


Figure 3.24 a plot of peak current (i_p) for silver-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing 5 × 10^{-9} M silver ions vs. the deposition time

Figure 3.25 and Figure 3.26 show the effect of preconcentration time on the voltammetric response studied using 5×10^{-10} M Ag^{+} solution (5.4×10^{-5} ppm). Peak currents centered at -0.00944 V are increased proportionally with time from 5 to 45 min. The value of peak potential provides the means of speciation while the peak current provides the means of quantitation.

The calibration curve for the stripping analysis of silver ion contained in 0.5 M H_2SO_4 solution was established in Figure 3.29. The calibration graph unequivocally indicates a linear relationship between the stripping peak currents and the deposition time with a regression coefficient of 0.9933.

The same stripping experiment was also performed on a 5×10^{-11} M Ag^{+} solution (5.4×10^{-6} ppm). It can be observed from Figures 3.27 and 3.28 that the peak current which was centered at -0.08472 V is increased, as the deposition time increased.

A linear relationship is observed between the anodic stripping peak current and the deposition time from 5 to 30 min with a regression coefficient of 0.9918 (Figure 3.30).

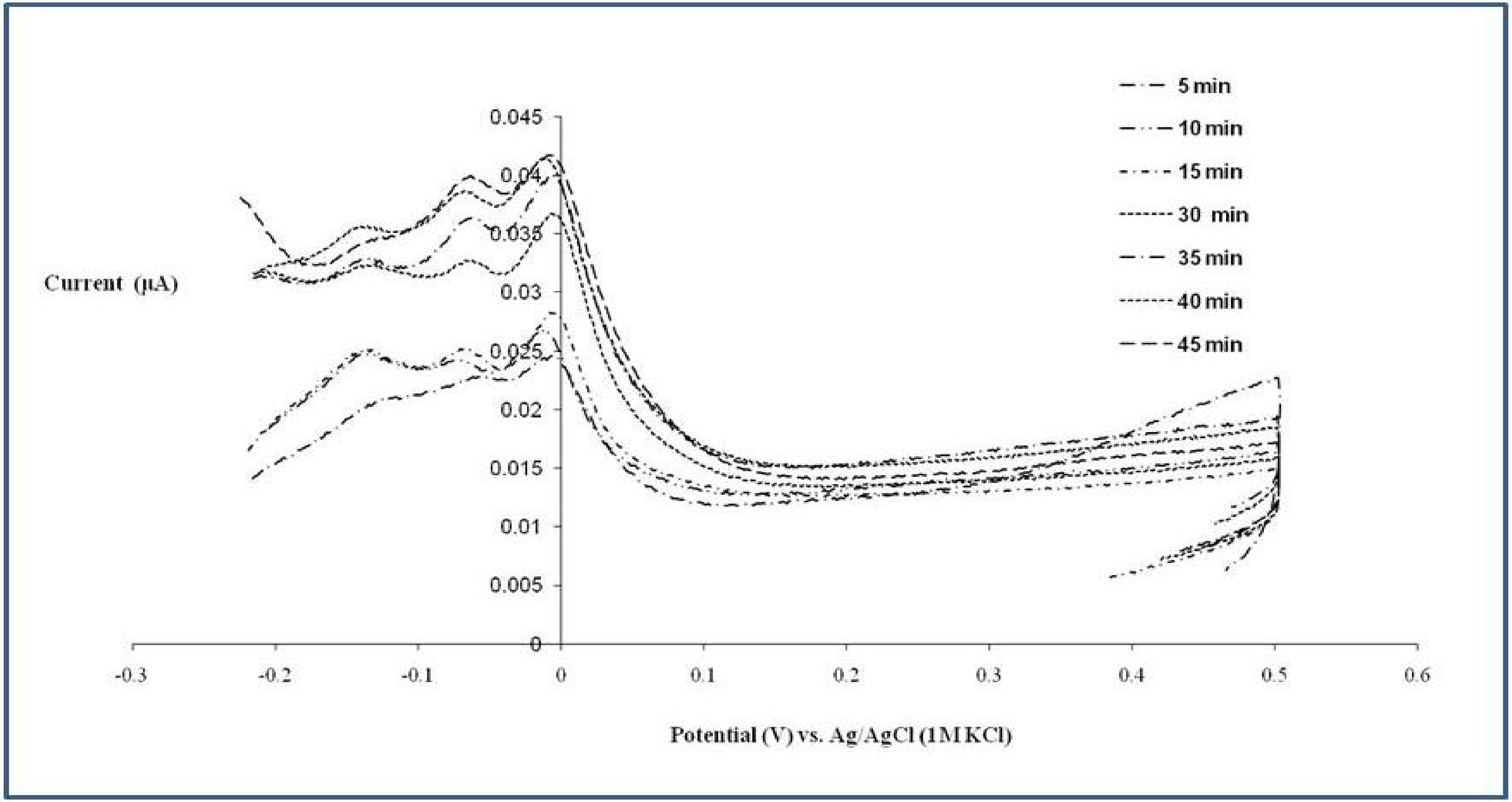


Figure 3.25 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-10} M Ag^{+} in 0.5 M H_2SO_4 at different deposition times

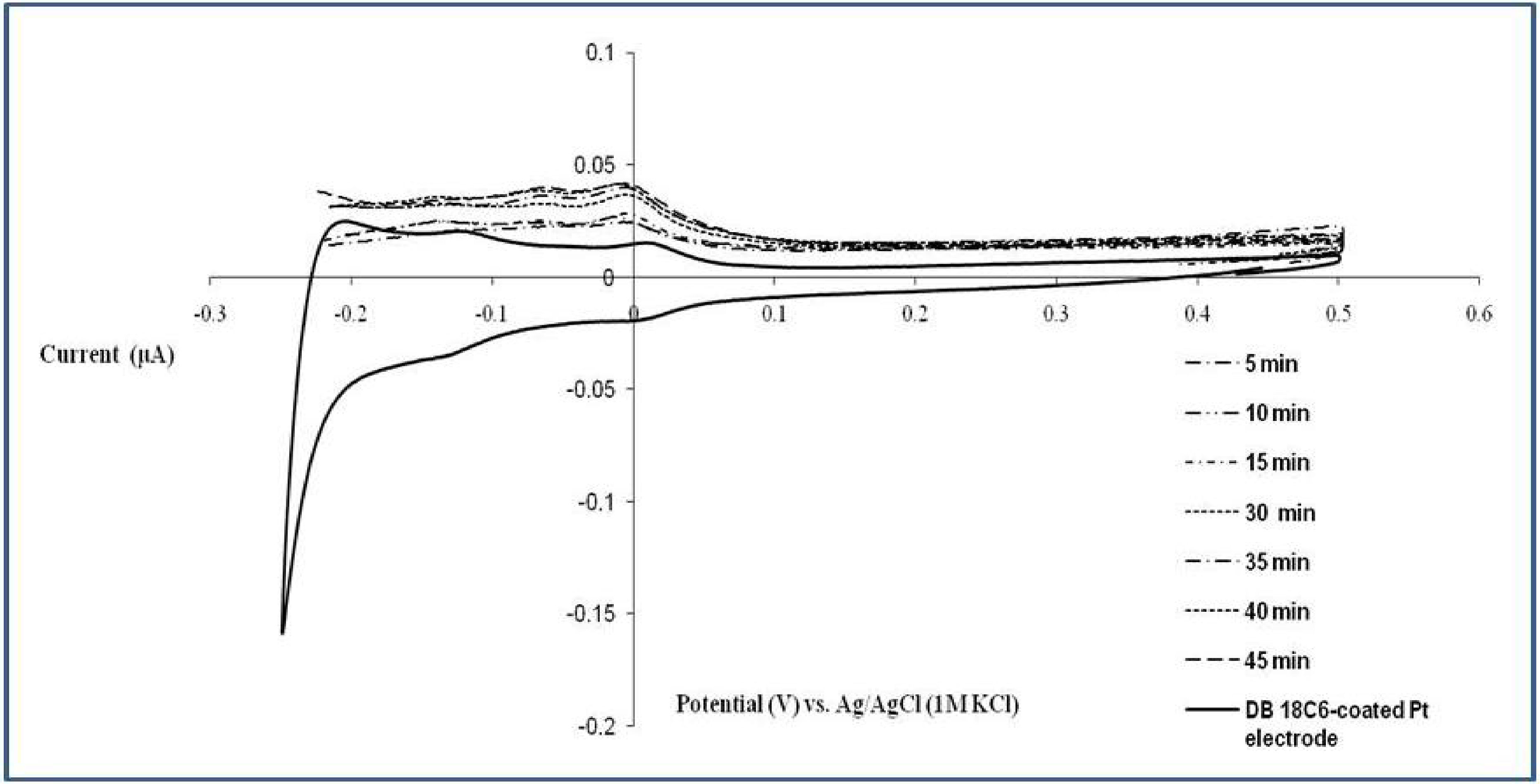


Figure 3.26 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-10} M Ag^{+} in 0.5 M H_2SO_4 at different deposition times (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

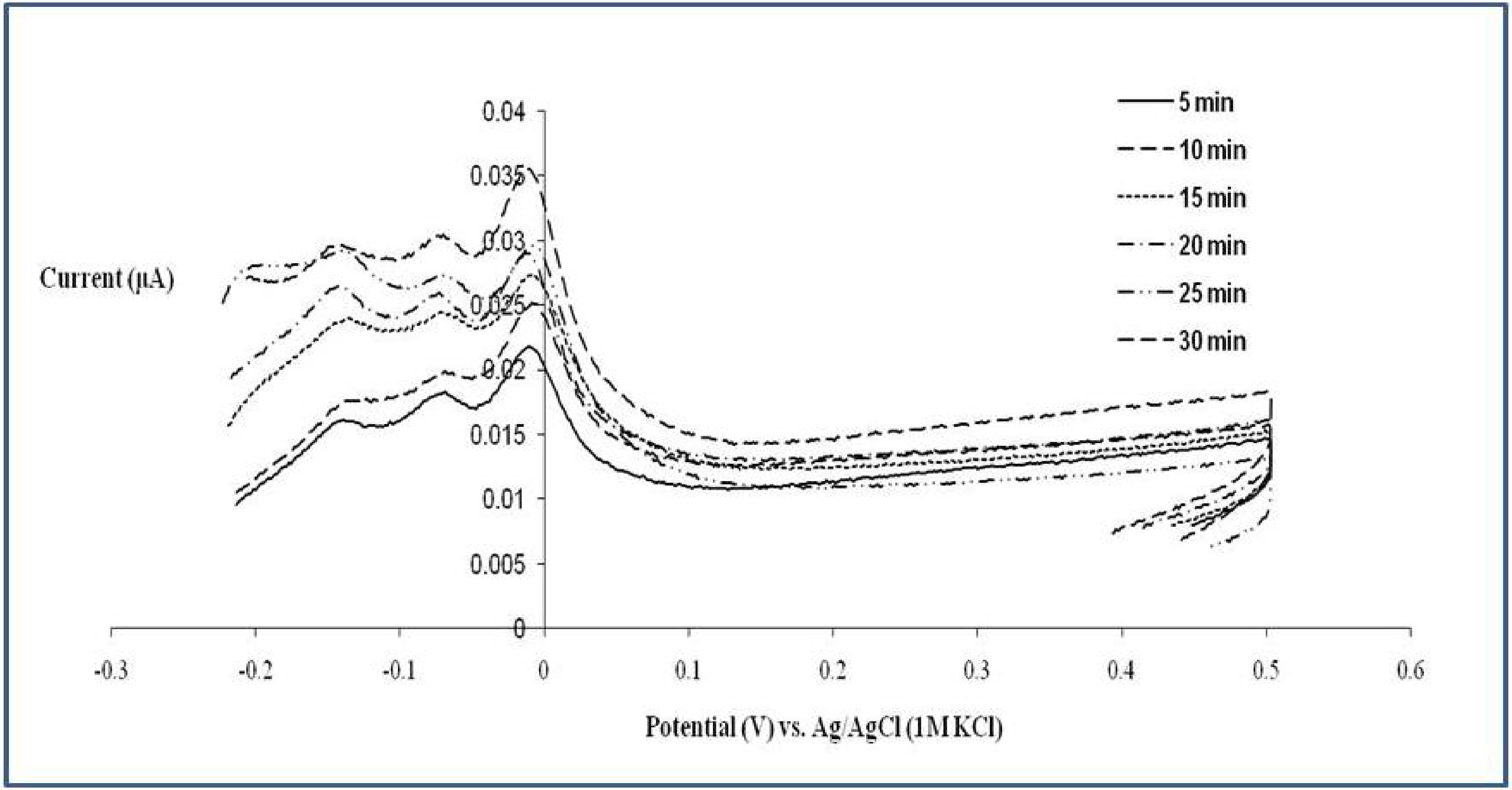


Figure 3.27 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-11} M Ag^+ in 0.5 M H_2SO_4 at different deposition times

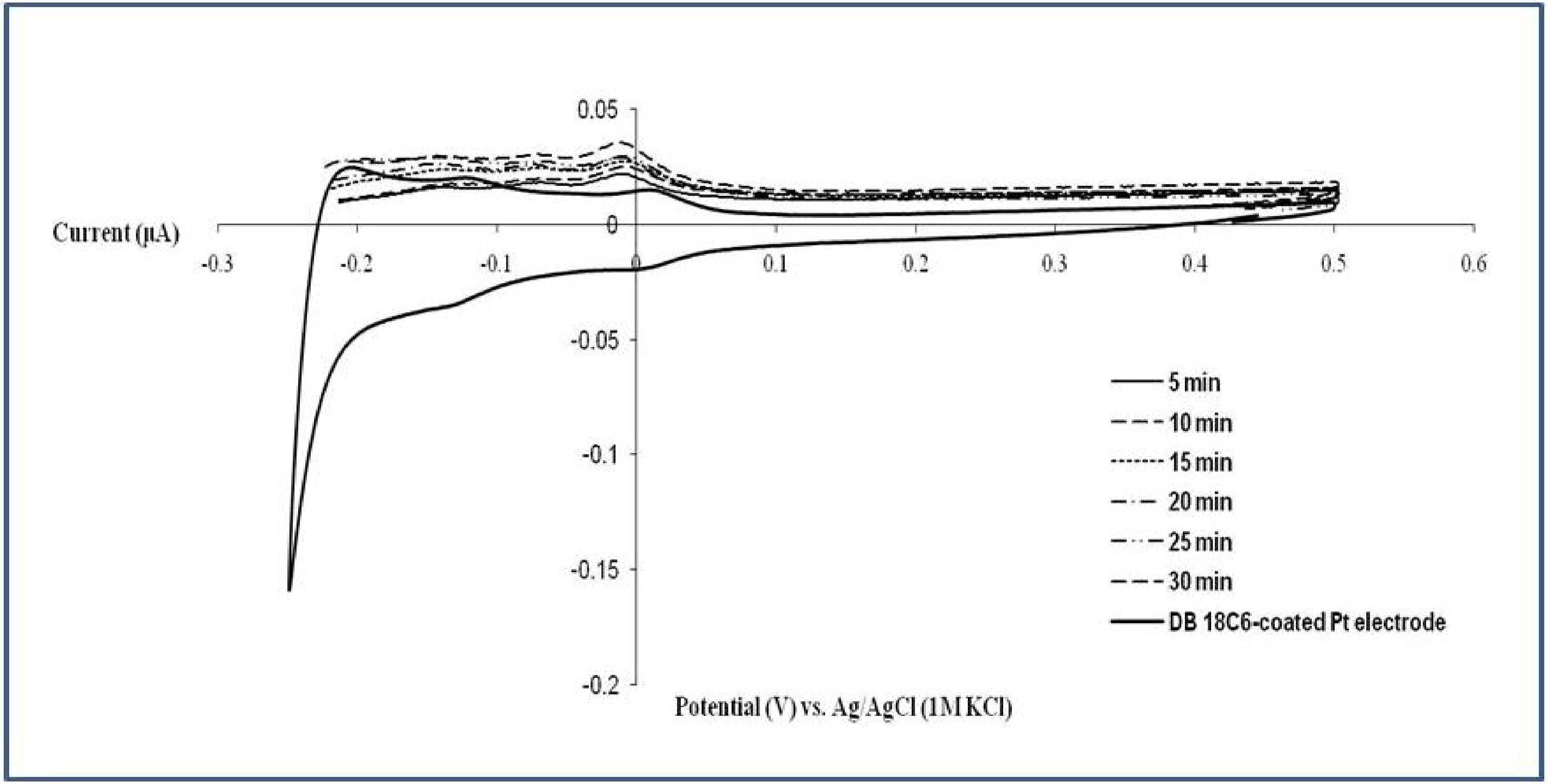


Figure 3.28 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-11} M Ag^{+} in 0.5 M H_2SO_4 at different deposition time (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

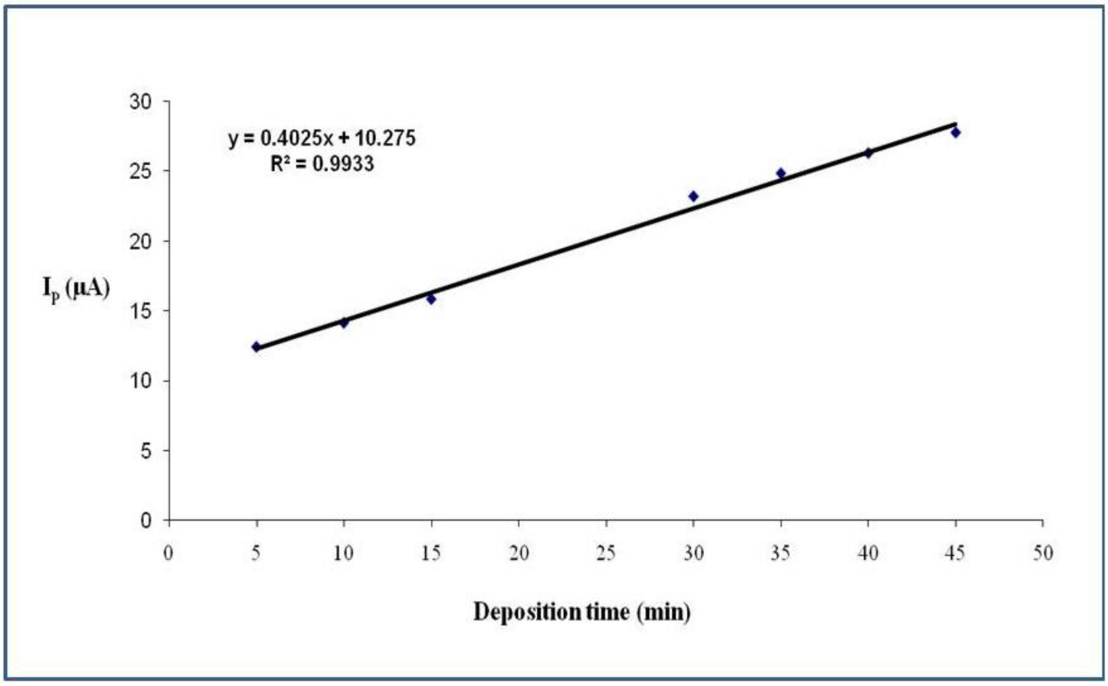


Figure 3.29 a plot of peak current (i_p) for silver-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing 5 × 10^{-10} M silver ions vs. the deposition time

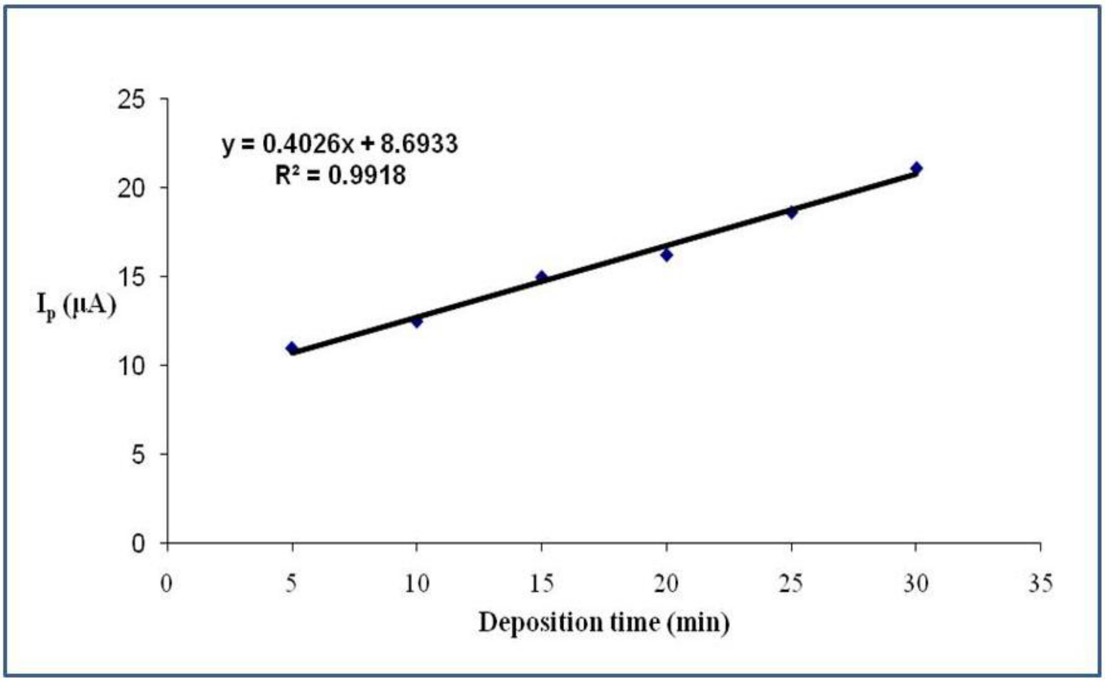


Figure 3.30 a plot of peak current (i_p) for silver-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing 5 × 10^{-11} M silver ions vs. the deposition time

In addition, anodic stripping voltammograms at different small concentrations of Ag (I) in parts per billion ranges (ppb) under optimum conditions (deposition time 10 min, scan rate 50 mV/s) are studied here for the first time. Form the best of knowledge, Won. et al 2007 have studied the determination of silver at carbon paste electrode(CPE) modified with N,N'-Diphenyl oxamide (DPO) by anodic stripping voltametry in range of 1×10^{-7}- 5×10^{-9} M at the deposition time of 10 min.

It can be shown In Figure 3.31 that the peak currents increased linearly with increasing concentrations of Ag^+ solution in the range of $5 \times 10^{-17} – 5 \times 10^{-12}$ M (5.4 $\times 10^{-9}– 5.4 \times 10^{-4}$ ppb).

A linear calibration graph was obtained between the log of peak current and the –log concentrations of Ag^+ with a regression coefficient of 0.9952 (Figure 3.33).

Figure 3.32 represents a comparison between the cyclic voltammogram of polycrystalline platinum electrode pretreated at open circuit for 10 min. with saturated Dibenzo-18-crown-6, and stripping peaks of different concentrations of silver at deposition time of 10 min.

In all Figures 3.19 - 3.22 and Figures 3.25-3.28, the first peak which was appeared to the right is due to the metal, which is here the silver, while the other two peaks which appeared to the left are due to the hydogen orientation on the platinum electrode, due to the fact that there orientation become clear and prominent when we deal with small concentrations in the range of ppb.

It is well known that the application of fast potential periodic routines on platinum rhodium, iridium, gold, or palladium produces permanent morphological changes with defined orientations, which depend on the potential limits and also metal

pretreatments produce crystallographic changes in the surface. Hydrogen adsorption covers the -0.25 to- 0.50V region here, showing two anodic peak contributions, which correspond to the different energetic states of the platinum/hydrogen bond (Zinola et al.,2003).

Though, the interaction of Pt with hydrogen has long been a hot subject for electrochemists, this seemingly simple system is by no means simple. Voltammetric and spectroscopic studies on this system reveal several controversies. Voltammetric studies on polycrystalline platinum electrodes and further on various single crystal platinum electrodes revealed details of the underpotential deposition (UPD) hydrogens. The two symetric peaks in the voltammogram of polycrystalline Pt electrodes in acid solution were attributed to the formation of strongly bound hydrogen (Hs) and weakly bound hydrogen (Hw). That (Hs) corresponds to hydrogen adsorbed at hollow sites, whereas(Hw) refers to hydrogen adsorbed at steps and defects (Tian et al., 1999).

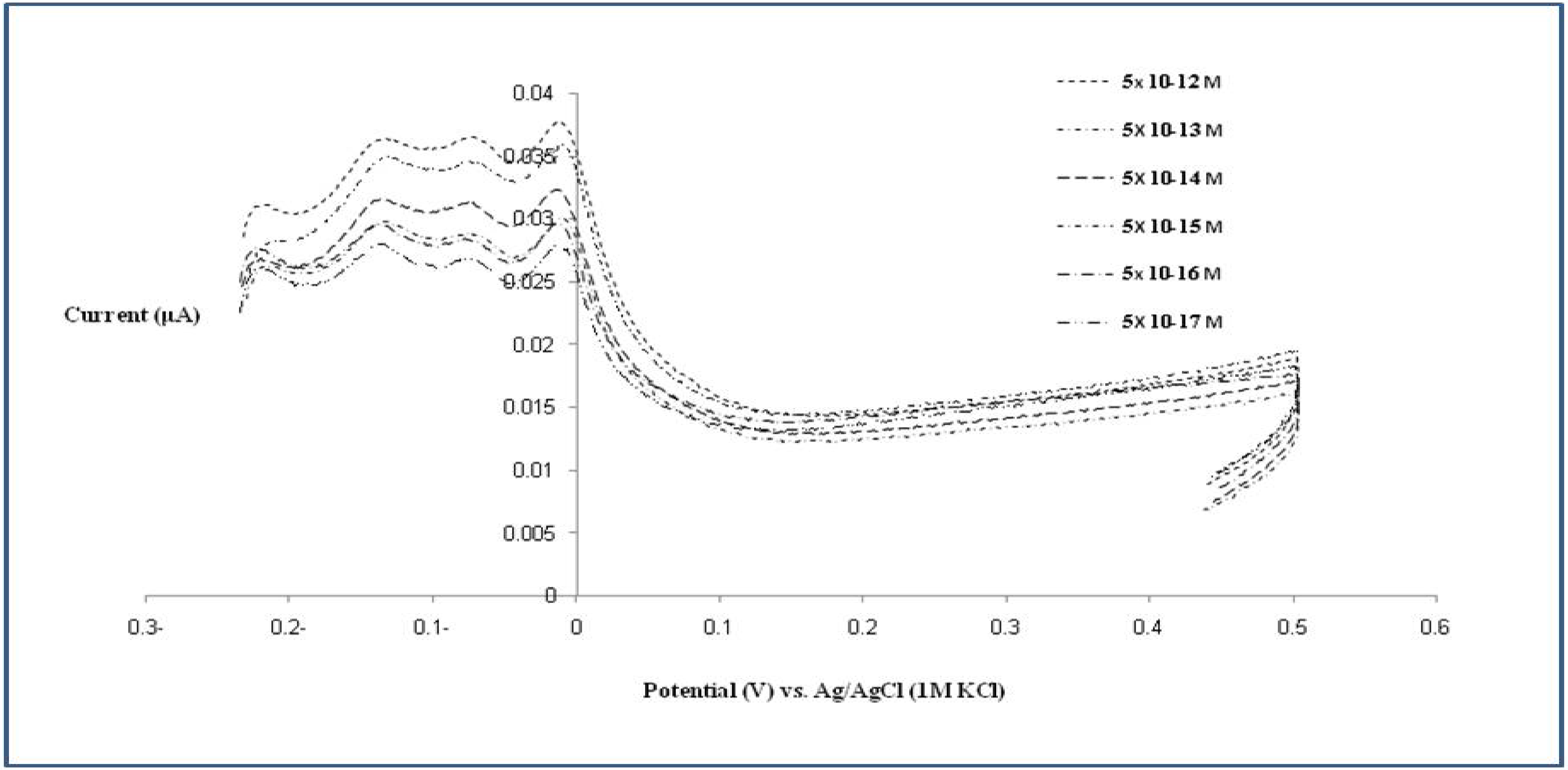


Figure 3.31 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of silver in 0.5 M H_2SO_4 (Deposition time 10 min, scan rate 50 mv/s)

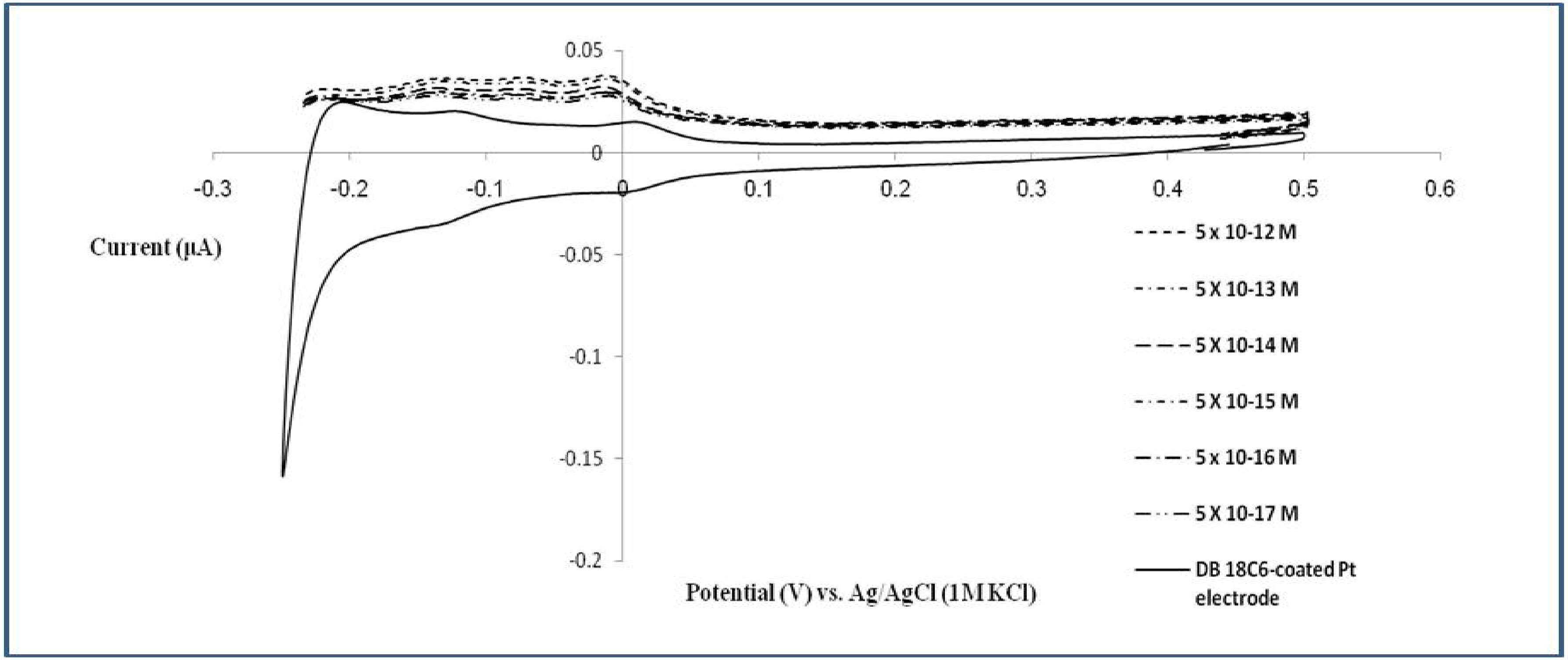


Figure 3.32 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of silver in 0.5 M H_2SO_4 at deposition time of 10 min (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

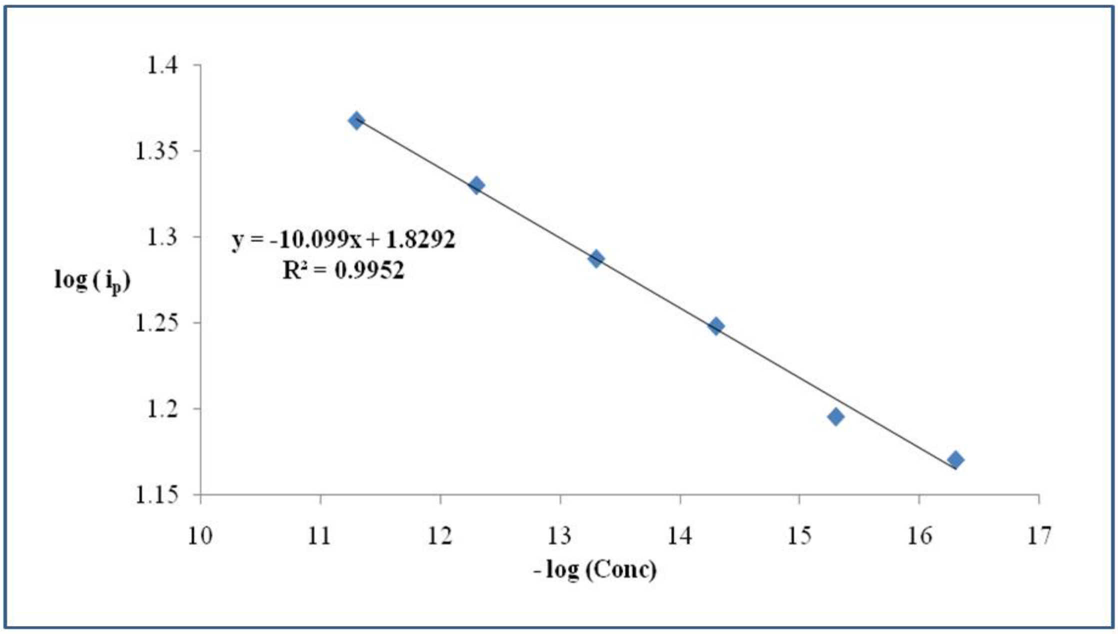


Figure 3.33 a plot of log peak current (i_p) for silver-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing different concentrations of silver solutions vs. the (- log) of these concentrations

3.4.2 Anodic stripping analysis of copper ions at a Modified polycrystalline platinum electrode

Copper is an essential trace element in biological systems. However, it contributes to water pollution in aquatics systems. Therefore, developing sensitive and selective methods for the determination of copper is of prime importance. Several analytical techniques have been employed in copper ion analysis, such as atomic absorption spectrometry (AAS), UV-spectrophotometry, atomic fluorescence spectrometry (AFS), X-ray Fluorescence, and inductively coupled plasma spectrometry (ICP). These techniques commonly are used for trace measurement of heavy metal ions in the laboratory and usually are not suitable for the task of in situ testing and monitoring. Expensive instrumentation and complicated sample preparation processes are also required. Electrochemical techniques are among the most favorable methods for the determination of heavy metal ions because of their low cost and high sensitivity (Oktem., et al 2011).

The modified platinum electrode was replaced in a cell which contained a purged solution of 5×10^{-5} M Cu^{2+} solution (3.177 ppm). The Pt electrode was held at a deposition potential -0.25V for a given length of time (5 min), then the working electrode was scanned in the positive direction (0.5 V) to strip of the copper from the modified electrode.

The same experiment was done by increasing the deposition time at 5 minutes intervals up to 35 min. Figures 3.34 and 3.35 show that the stripping peak currents increased linearly with the preconcentration time from 5 to 35 min.

A linear relationship is observed between the anodic stripping peak currents and the deposition times with a regression coefficient of 0.9932 (Figure 3.38).

Anodic stripping voltammograms at different concentrations of Cu^{2+} under optimum conditions (deposition time 10 min, scan rate 50 mV/s) are shown in Figure 3.36. The peak current increased linearly with decreasing concentrations of Cu^{2+} solution in the range of 5×10^{-11} - 5×10^{-15} M ($3.18 \times 10^{-3} – 5.4 \times 10^{-7}$ ppb).

A linear calibration graph was obtained between the peak current and the –log concentrations of Cu^{2+} with a regression coefficient of 0.989 (Figure 3.39).

Figure 3.37 represents a comparison between the cyclic voltammogram of polycrystalline platinum electrode pretreated at open circuit for 10 min. with saturated Dibenzo-18-crown-6, and stripping peaks of different concentrations of copper at deposition time of 10 min.

In the two Figures 3.36 and 3.37 the first peak which was appeared to the right is due to the metal, which is here the copper, while the other two peaks which appeared to the left are due to the hydogen orientation on the platinum electrode, due to the fact here that there orientation become clear and prominent when we deal with small concentrations in the range of ppb.

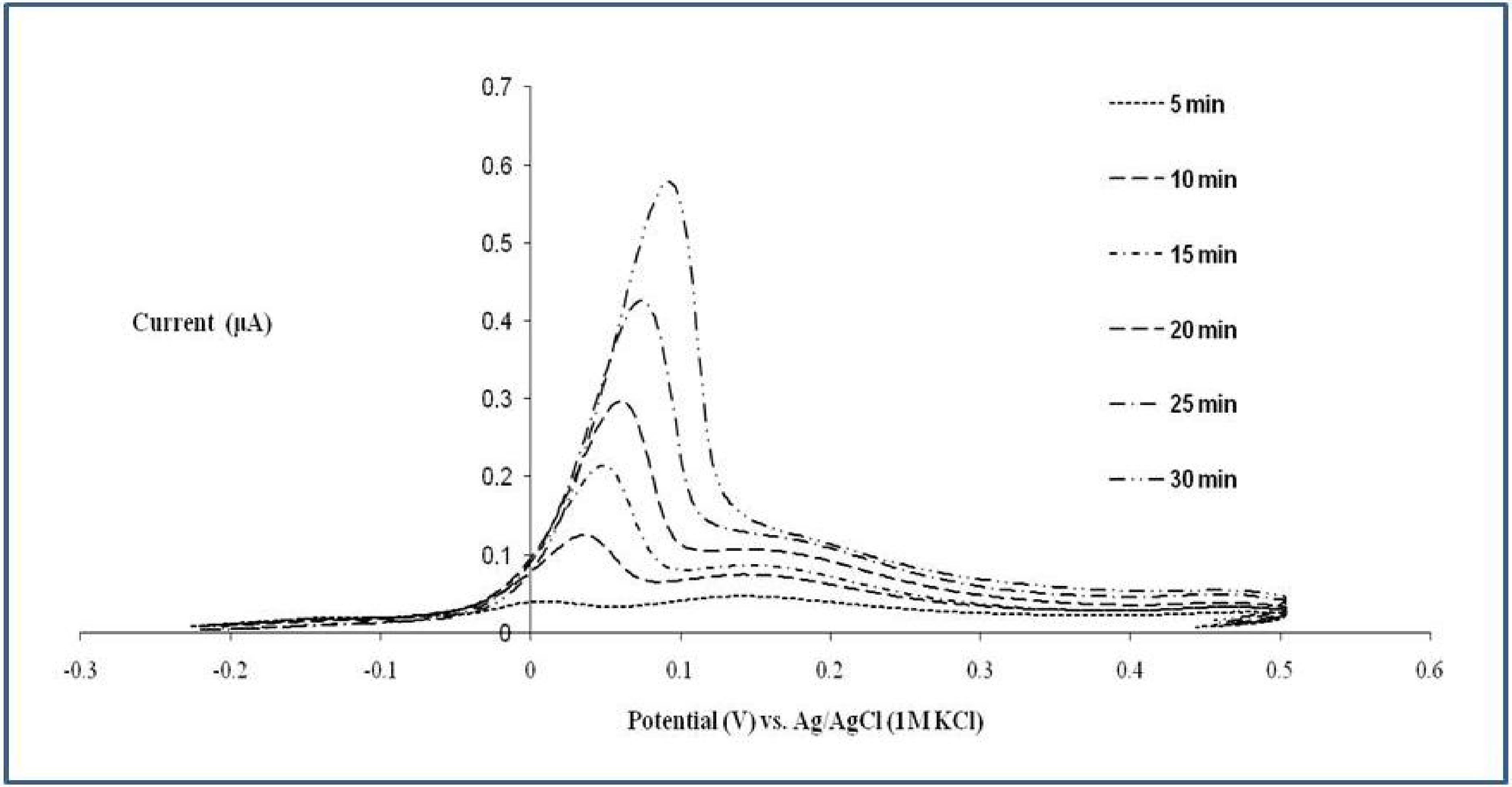


Figure 3.34 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-5} M Cu^{2+} in 0.5 M H_2SO_4 at different deposition time

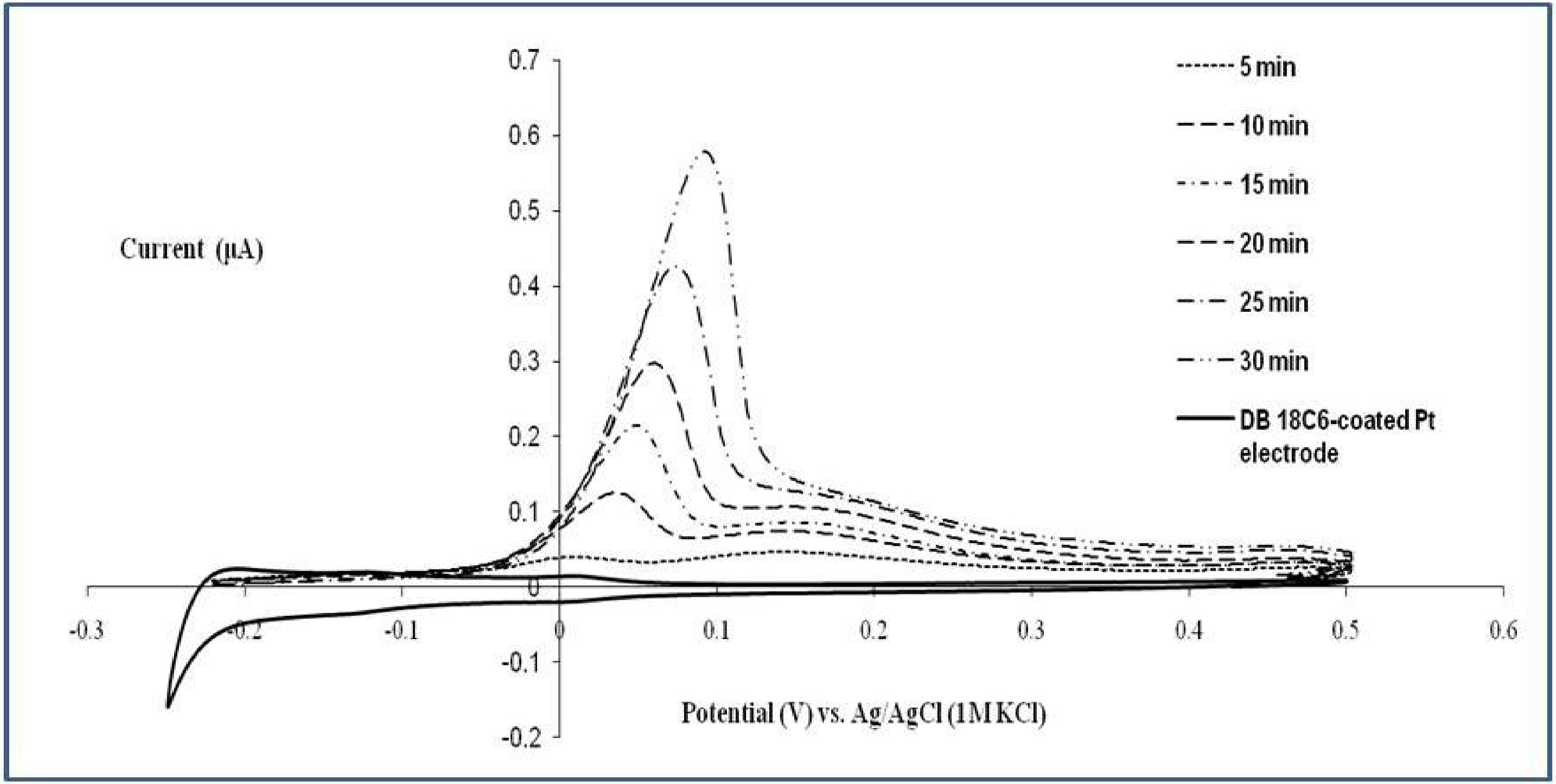


Figure 3.35 Cyclic voltammogram of modified polycrystalline platinum electrode in solution of 5 × 10^{-5} M Cu^{2+} in 0.5 M H_2SO_4 at different deposition time (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

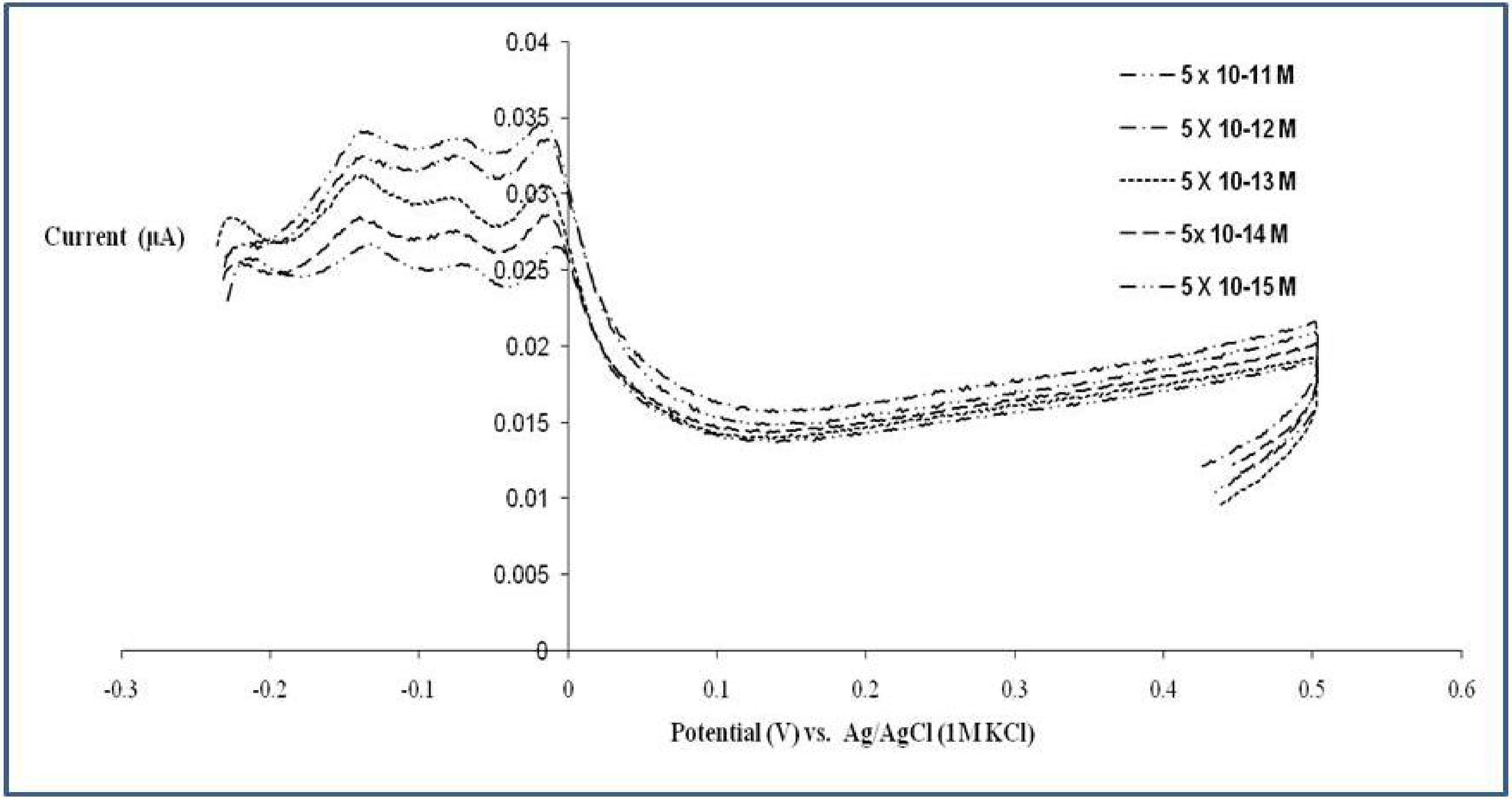


Figure 3.36 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of copper in 0.5 M H_2SO_4 (Deposition time 10 min, scan rate 50 mv/s)

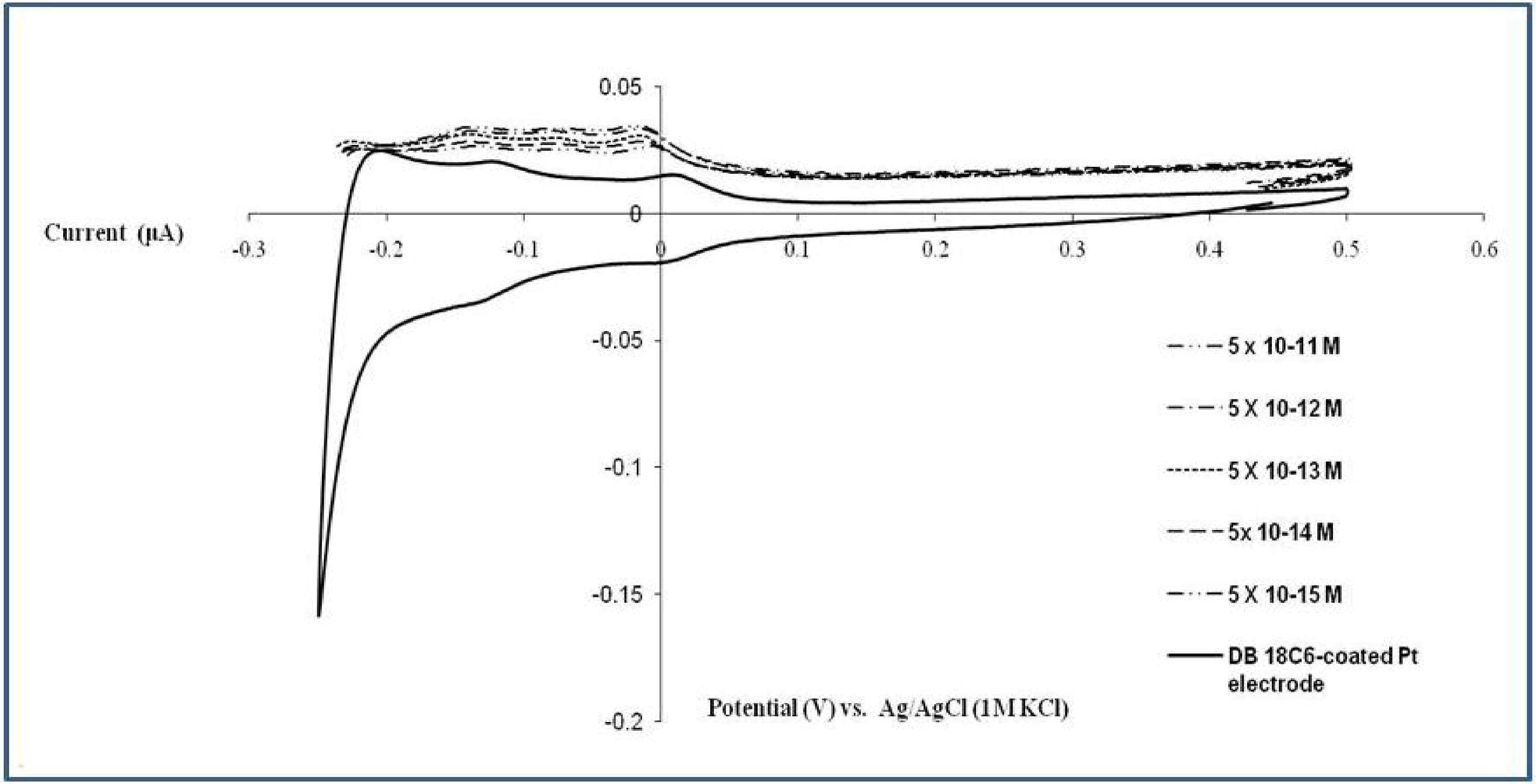


Figure 3.37 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of copper in 0.5 M H_2SO_4 at deposition time of 10 min (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

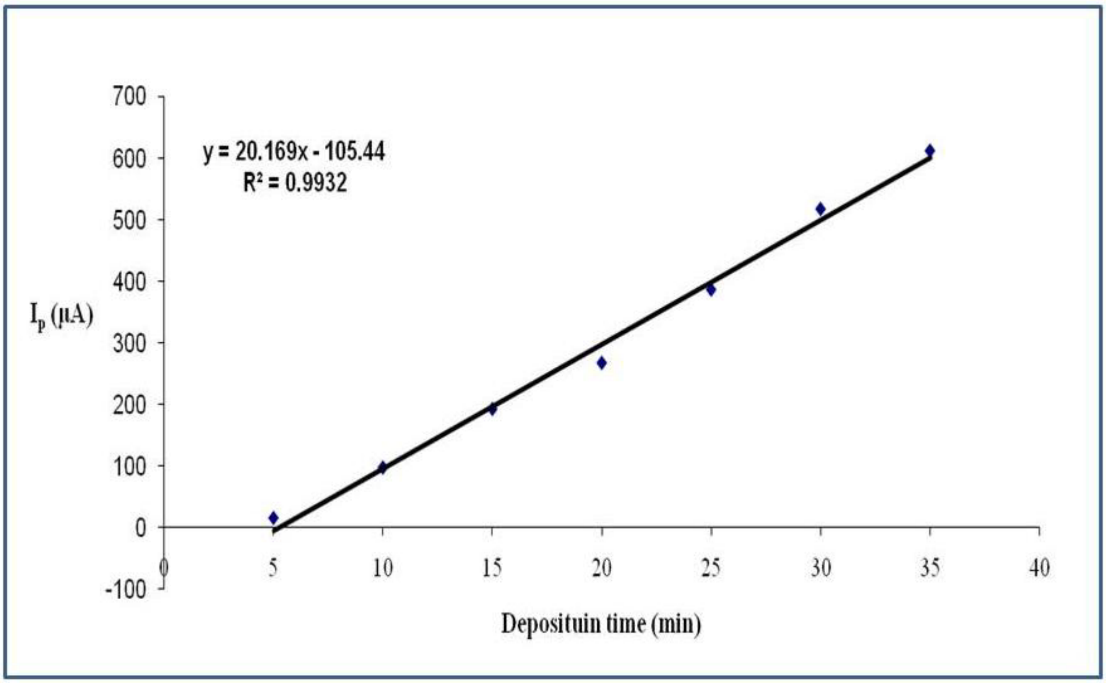


Figure 3.38 a plot of peak current (i_p) for copper-stripping from DB 18C6-coated platinum electrode in 0.5 M H_2SO_4 containing 5 × 10^{-5} M copper ions vs. the deposition time

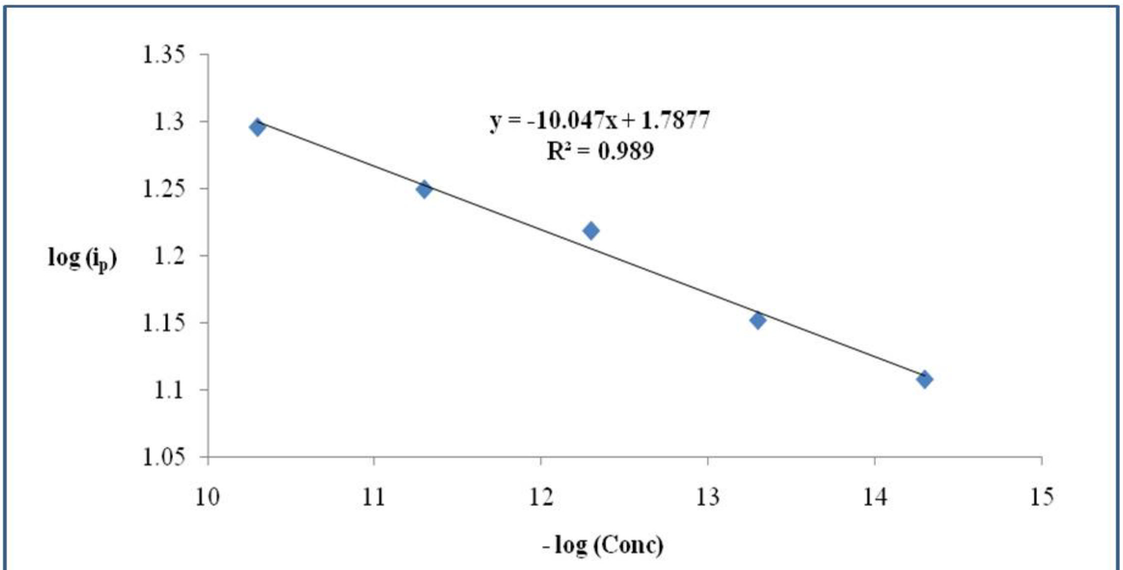


Figure 3.39 a plot of log peak current (i_p) for copper-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing different concentrations of copper solutions vs. the (- log) of these concentrations

3.4.3 Anodic stripping analysis of Nickel ions at a modified polycrystalline platinum electrode

Pure nickel shows a significant chemical activity, but it reacts slowly at ambient conditions due to the formation of a protective oxide surface. Historically it has been used for plating metals such as iron and brass, for chemical apparatus, and in certain alloys such as German silver. Nickel was a common component of coins, but it has largely been replaced by cheaper iron for this purpose, especially since the metal has proved to be a skin allergen for some people.

As mentioned above each cycle of experiments was commenced by obtaining a verified-clean platinum surface, followed by modification with crown ether verified by duplication of the voltammogram for DB 18C6 –coated surface in a DB 18C6-free 0.5 M sulfuric acid solution.

The modified platinum electrode was replaced in a cell which contained a purged solution of 5×10^{-11} M Ni^{2+} solution (2.94×10^{-3} ppb).The Pt electrode was held at a deposition potential for a given length of time (10 min), then the working electrode is scanned in the positive direction (0.5 V) to remove the nickel from the electrode.

The same experiment was done by decreasing the concentrations of nickel solution up to 5×10^{-15} M. From Figure 3.40 it can be observed that the peak current increased linearly with increasing the concentrations of Ni^{2+} solution in the range of 5×10^{-15} - 5×10^{-11} M (2.94×10^{-3}– 2.94×10^{-7} ppb).

A good linear relationship was obtained between the log of peak current and the- log concentrations of Ni^{2+} with a regression coefficient of 0.9931 (Figure 3.44).

Figure 3.41 represents a comparison between the cyclic voltammogram of polycrystalline platinum electrode pretreated at open circuit for 10 min. with saturated Dibenzo-18-crown-6, and stripping peaks of different concentrations of nickel at deposition time of 10 min.

3.4.4 Anodic stripping analysis of Cadmium ions at a modified polycrystalline platinum electrode

The determination of cadmium is important due to its toxicity. It inters water bodies through wastewater from metal plating industries, nickel cadmium batteries, phosphate fertilizers, mining, pigments stabilizers and alloys.

The modified electrode was preconcentrated in solutions with different Cd (II) concentrations at −0.25 V for 10 min. From Figure 3.42 it can be observed that the peak current values increase with increasing concentrations of Cd^{2+} in the range of 5×10^{-15} - 5×10^{-11} M (5.64×10^{-7}– 5.64×10^{-3} ppb).

Figure 3.45 shows a liner curve between the log of stripping peak current and the -log concentrations of Cadmium in 0.5 M H_2SO_4 solution with a regression coefficient of 0.9877.

Figure 3.43 represents a comparison between the cyclic voltammogram of polycrystalline platinum electrode pretreated at open circuit for 10 min. with saturated Dibenzo-18-crown-6, and stripping peaks of different concentrations of cadmium at deposition time of 10 min.

In addition, in the figuers from 3.40 to 3.43 the first peak which was appeared to the right its due to the metal, which is here for nickel and cadmium respectively, while the other two peaks which appeared to the left are due to the hydogen orientation on the platinum electrode. They become important in much smaller concentrations.

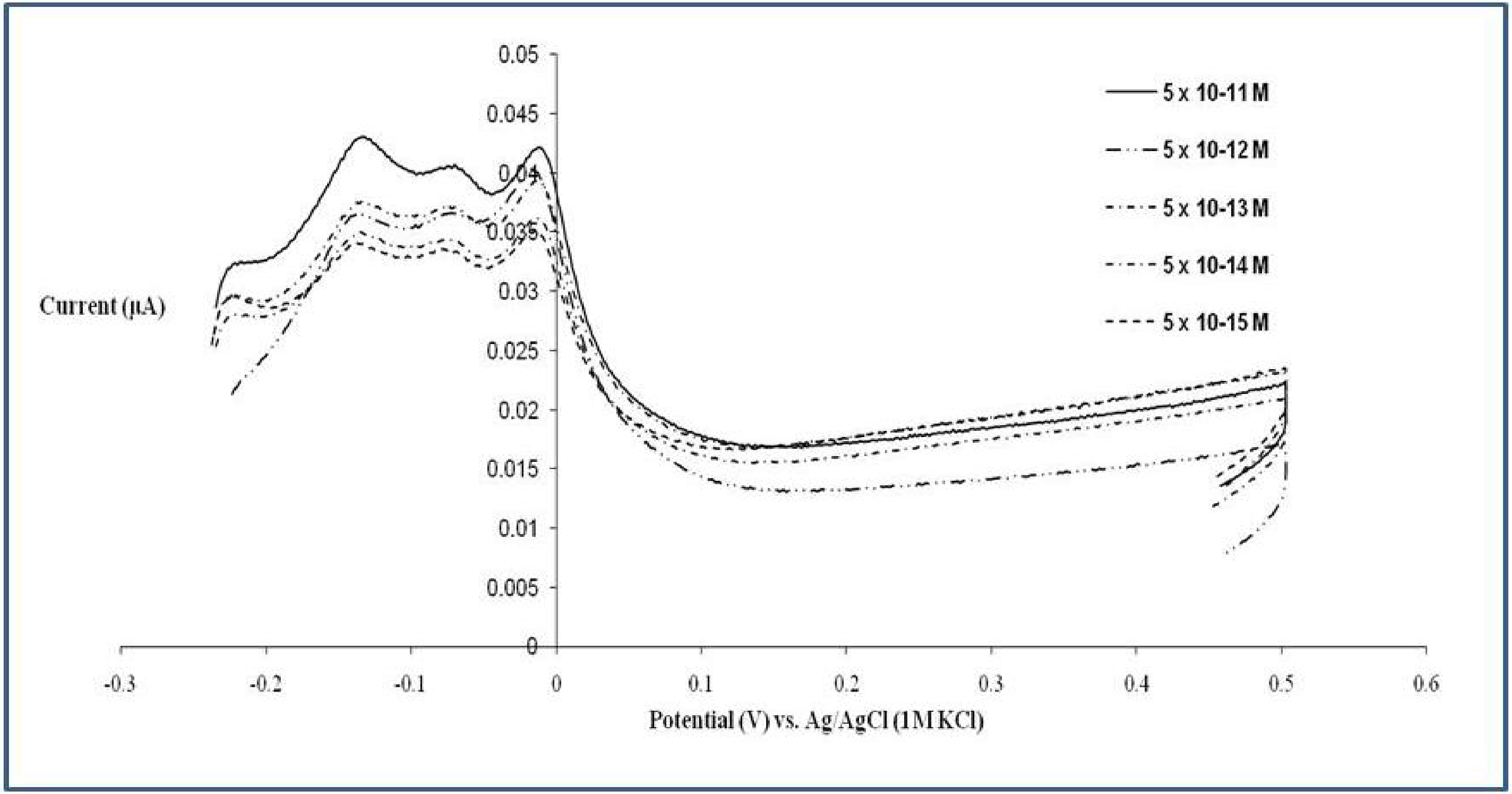


Figure 3.40 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of nickel in 0.5 M H_2SO_4 (Deposition time 10 min, scan rate 50 mv/s)

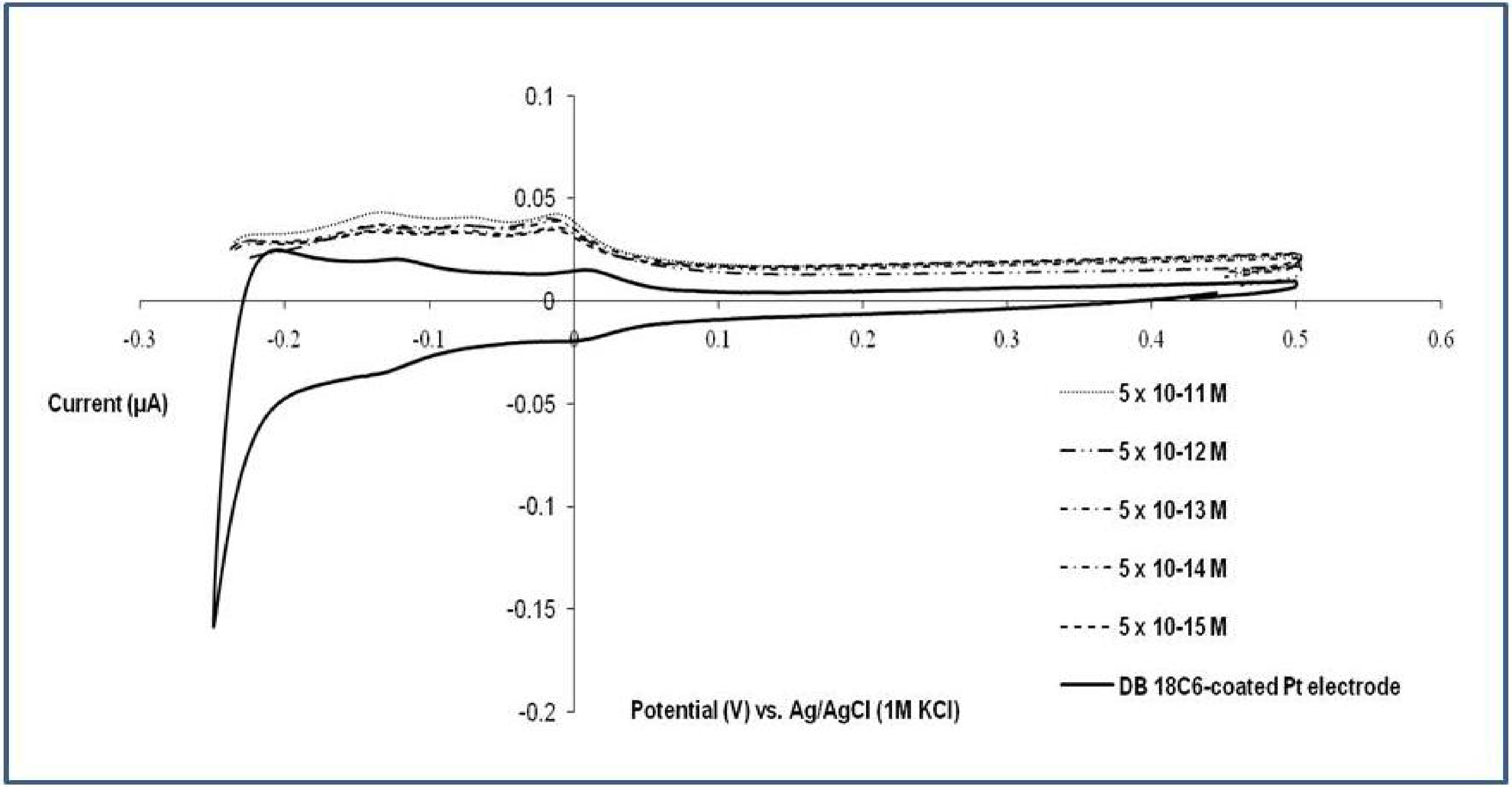


Figure 3.41 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of nickel in 0.5 M H_2SO_4 at deposition time of 10 min (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

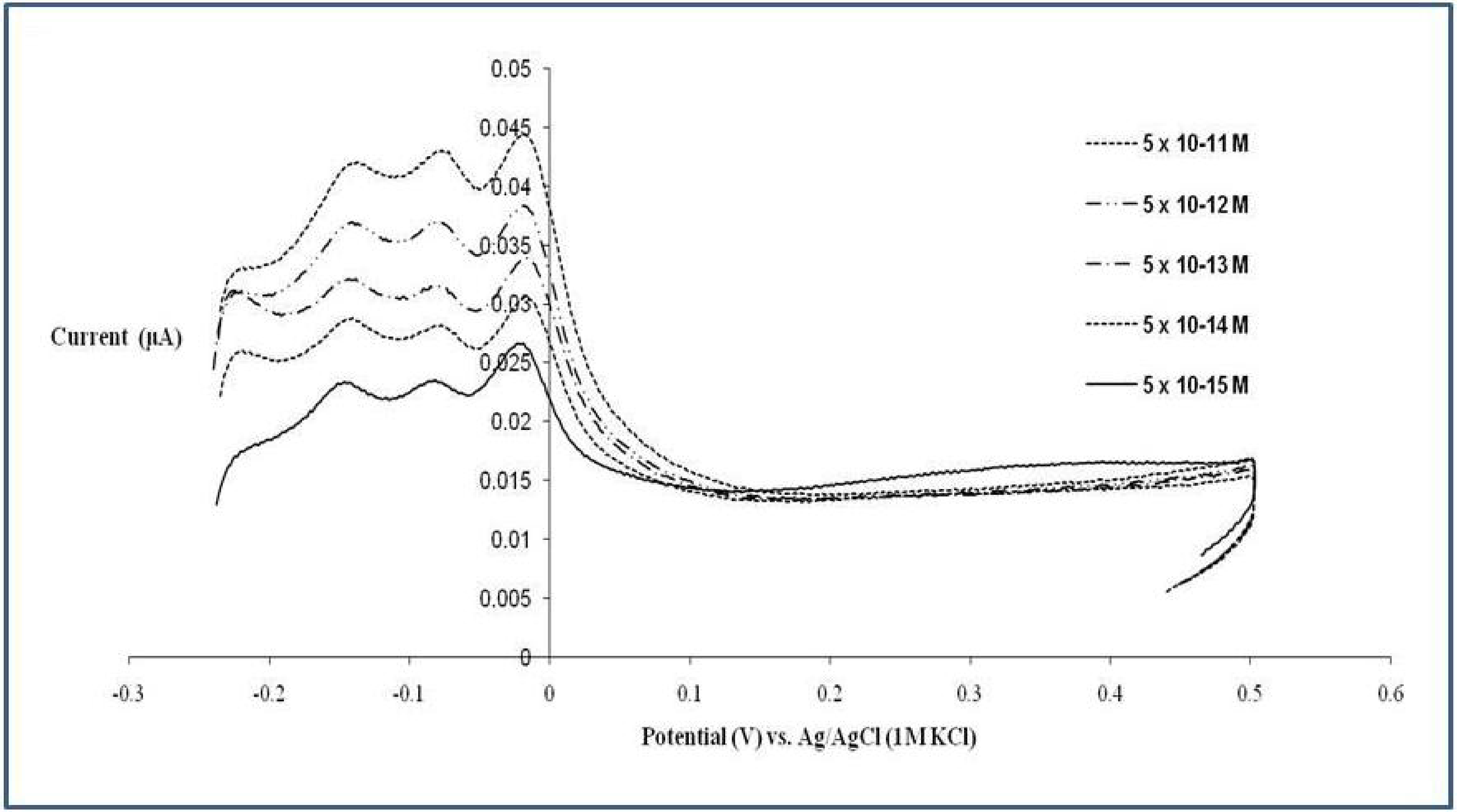


Figure 3.42 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of cadmium in 0.5 M H_2SO_4 (Deposition time 10 min, scan rate 50 mv/s)

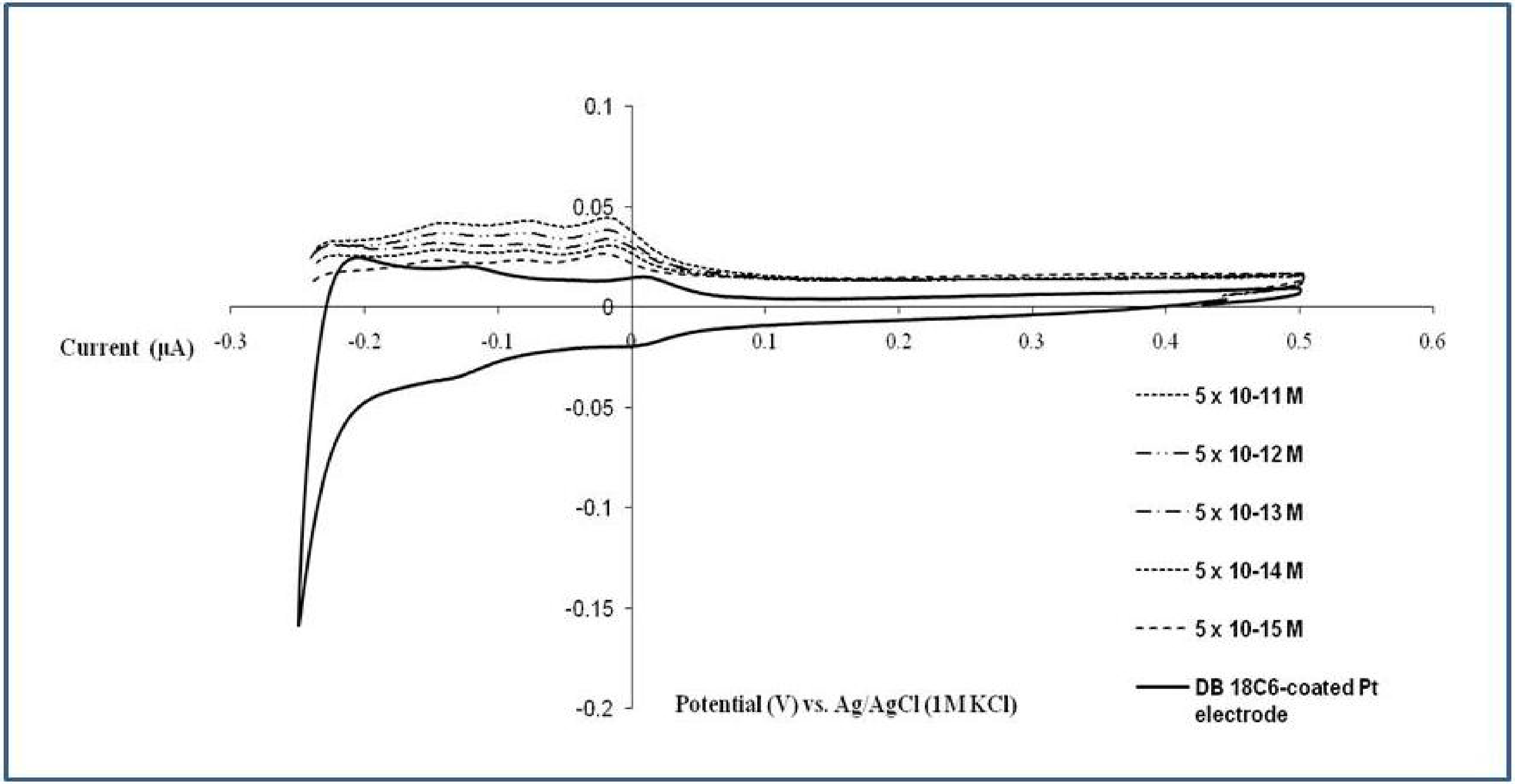


Figure 3.43 Cyclic voltammogram of modified polycrystalline platinum electrode in different concentrations of cadmium in 0.5 M H_2SO_4 at deposition time of 10 min (discreet lines). Cyclic voltammogram of modified polycrystalline platinum electrode in 0.5 M H_2SO_4 solution (solid line)

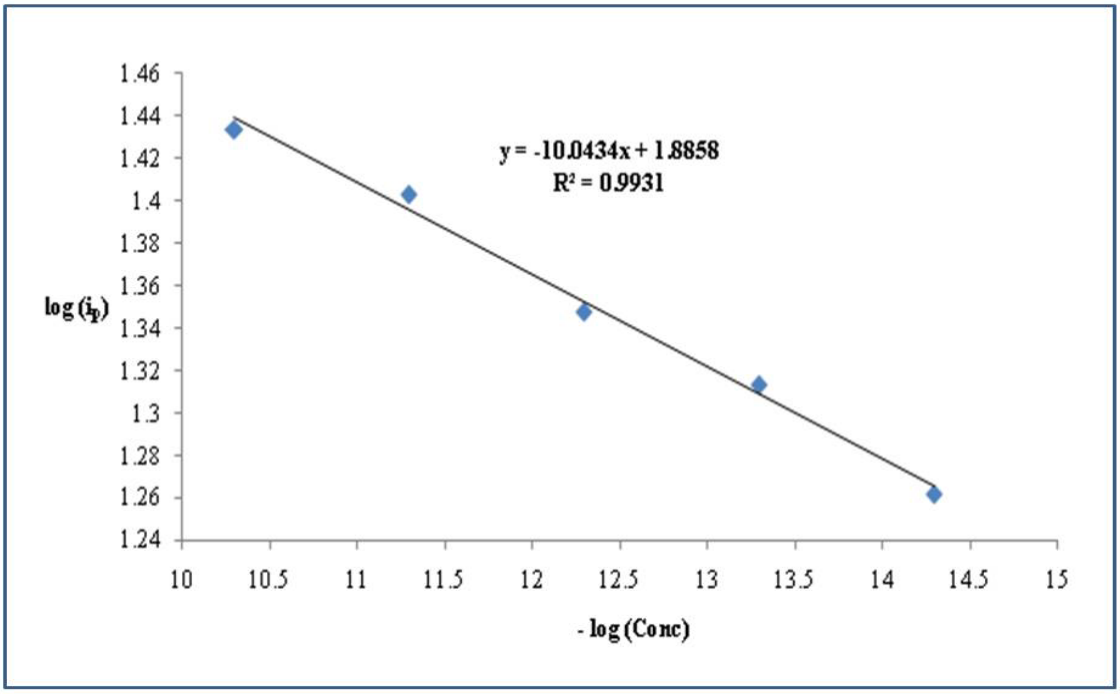


Figure 3.44 a plot of log peak current (i_p) for nickel-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing different concentrations of nickel solutions vs. the (- log) of these concentrations

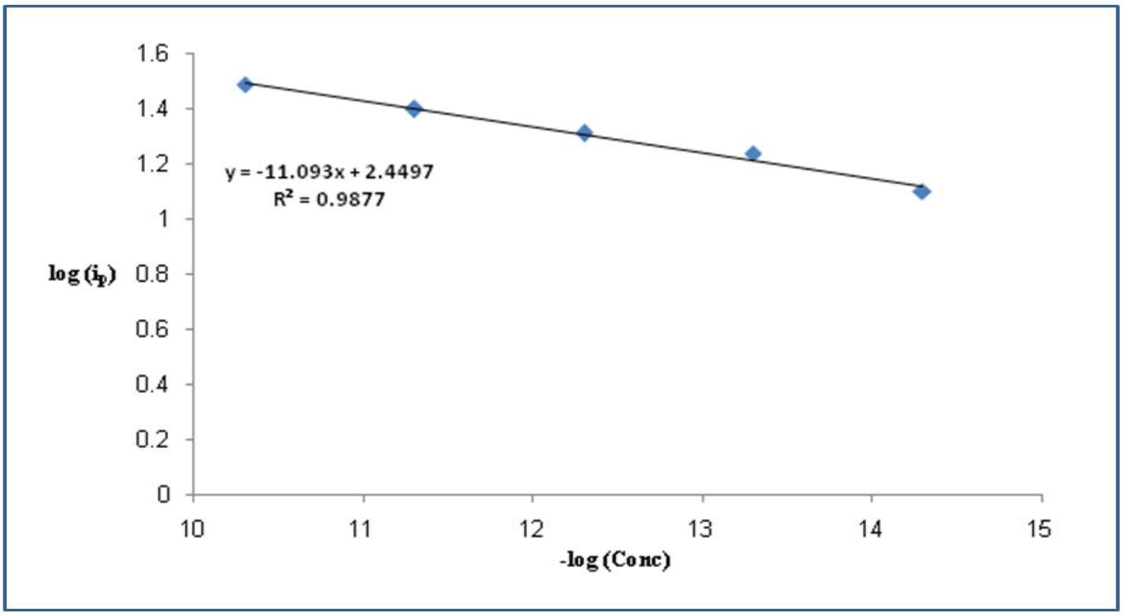


Figure 3.45 a plot log of peak current (i_p) for cadmium-stripping from DB 18 C6-coated platinum electrode in 0.5 M H_2SO_4 containing different concentrations of cadmium solutions vs. the (- log) of these concentrations

3.5 Determination of Cu concentration in a brazing alloy Sample by AAS and comparison with anodic stripping voltammetry

A 0.5 g of an alloy sample, was washed and dissolved in small volume of nitric acid (Since this is a trace analysis technique, all glassware was rinsed thoroughly before use with nitric acid and ultra-pure water to minimize contamination), then it was diluted with triply-distilled water to 500 ml volumetric flask, after that 10 ml of this solution was taken and diluted with water in 100 ml volumetric flask, finally 10 ml aliquot of this solution was taken and diluted with water in 250 ml volumetric flask.

From 1000 ppm Cu standard solution, four samples (2.5, 5, 10, 20 ppm) were prepared and analyzed by AAS along with the brazing alloy sample.
Table 1 shows these concentrations plus the concentration of copper in the alloy which was determined by AAS.

It was observed that the concentration of the copper in the alloy sample was to be 3.3 ppm i.e. 5.19×10^{-5} M. Figure 3.46 shows the calibration curve for the concentration of copper in the standard solutions and its concentration in the alloy. A linear relationship between the concentration of copper and the absorbance was obtained with a regression coefficient of 0.986.

So as it was shown that there are not statistical differences between the results obtained by both methods. These results indicate that the developed electrode can be successfully employed to reliable copper determination in samples without any sample pretreatment.

Table 1. Concentrations of copper in standard solutions and in alloy sample vs. absorbance in AAS

SAMPLE	CONC ppm	% RSD	MEAN ABS
blank	0.00		0.00
Standard 1	2.5	0.5	0.200
Standard 2	5.0	0.4	0.398
Standard 3	10.0	0.3	0.798
Standard 4	20.0	0.2	1.294
Alloy sample	3.3	0.4	0.266

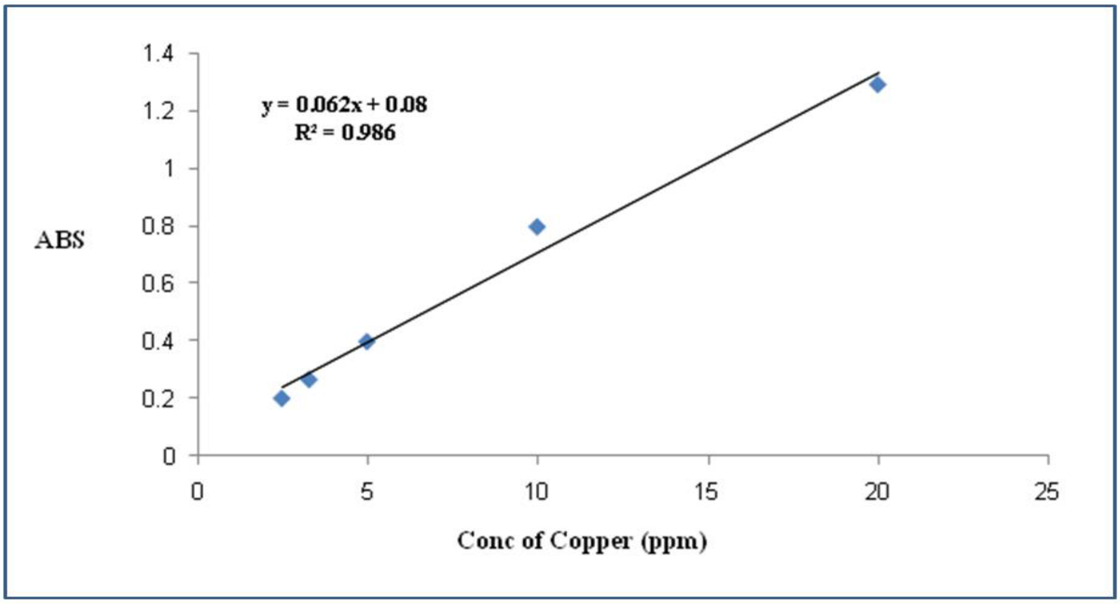


Figure 3.46 Calibration curve for AAS; relation between the concentration of copper (in standard solutions and in an alloy sample) and the absorbance

3.4.5. Detection limit for the stripping analysis metals (Ag^{+}, Cu^{2+}, Ni^{2+} and Cd^{2+})

The limit of detection (LOD) was calculated on the peak current using the following equations:

$$S_m = \bar{S}_{bl} + ks_{bl}$$

Where,

S_m = analytical signal, I_p

$\bar{S}_{bl}$ = mean of blank signal (twenty runs)

k = constant which equal 3

s_{bl} = standard deviation of the blank

And

$$c_m = \frac{S_m - \bar{S}_{bl}}{m}$$

c_m = detection limit

m = slope

The detection limits for the analyzed metals by anodic stripping technique are summarized in table 2.

Table 2: Detection limits for the anodic stripping analysis of Silver, Copper, Nickel and Cadmium (Deposition time =10 min)

Metal	Concentration range $mol.L^{-1}$	Detection limit $mol.L^{-1}$	Detection limit (ppb)
Silver	$5 \times 10^{-12} – 5 \times 10^{-17}$	1.68×10^{-16}	1.81×10^{-8}
Copper	$5\times 10^{-11} – 5 \times 10^{-15}$	1.43×10^{-16}	9.09×10^{-9}
Nickel	$5\times 10^{-11} – 5 \times 10^{-15}$	1.59×10^{-16}	9.33×10^{-9}
Cadmium	$5\times 10^{-11} – 5 \times 10^{-15}$	7.08×10^{-17}	7.99×10^{-9}

4. CONCLUSIONS AND RECOMMENDATIONS

Surface electro-chemistry investigation showed that DB 18C6 adlattic on platinum electrodes is highly stable, it is not desorbed by rinsing, and repetitive cyclization of the electrode potential between hydrogen evolution and DB 18C6 oxidation limits.

The adsorbate covers about of 71.1% and 68.0% on atomic basis of the platinum electrodes on wire and RDE surface respectively. The crown ethers adsorb chemically intact in a limited potential region between 500 and -250 mV vs. Ag/AgCl.

A chemically modified polycrystalline platinum wire and rotating disk platinum electrodes have been developed using DB 18C6 for the determination of Ag (I) and Cu (II) by cyclic voltammetry. The electrode offers simplicity in preparation, high stability and high selectivity to determine these ions. A good linear relationship between the concentrations of these ions and the peak current was obtained.

The DB 18C6-coated rotating disk platinum electrode was used to study the relationship between the angular velocity $\omega^{1/2}$ and the peak current of these two metals. A good linear relationship was obtained between the peak current and the $\omega^{1/2}$ of silver and copper respectively.

Electrochemical sensors based on stripping voltammetry appear to be a promising technique for determining aqueous heavy metal concentrations. These sensors are usually sensitive, compact, low cost, and easily integrated into field-deployable units.

In the present piece of work, the modified Pt electrode was used in anodic stripping analysis of silver, copper, nickel and cadmium ions.

An excellent linear relationship between the anodic stripping peak current and the concentration of these metals was obtained in 0.5 M H_2SO_4 solution.

In addition, a concentration of copper in an alloy sample was determined by AAS and compared with an anodic stripping voltammetry. The peak current signal of Cu (II) was not so different from the previous results and there is a correlation between the AAS and the electrochemical method.

For further work it is recommended to try these modified electrodes as electrochemical detectors in HPLC for the analysis of some metal ions.

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التحليل الإنتزاعي و الهيدروديناميكي لكينونات أيونية على قطب البلاتين المعدل بإيثر ثنائي بنزو – 18– تاج-6

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ملخص

لقد دلت الإختبارات الفولتامترية أن أقطاب البلاتين عديدة البلورة المعدلة بطبقة من الإيثر التاجي (ثنائي بنزو 18-تاج-6) تتمتع بخمول عال تجاه الإمتزاز الجزيئي , الأمر الذي يعني استئصال العمليات السطحية والتفاعلات الدخيلة. حيث تم تحضير هذه الأقطاب بغمسها في محلول الإيثر التاجي عند ظرف دائرة مفتوحة ثم دراسة الثبات الكيميائي لتلك الإيثرات التاجية على تلك الأقطاب في محلول حمض الكبريتيك ٠,5 مول/لتر . حيث أظهرت أقطاب البلاتين المعدلة ثباتا في الفولتية ما بين ٠,5 ← -0.25 فولت.

تم تحليل أيونات الفضة و النحاس بإستخدام تقنية الفولتامترية الحلقية على نوعين من أقطاب البلاتين المعدلة بطبقة من الإيثر التاجي وهما قطب البلاتين الثابت وقطب القرص الدوار. حيث أثبتت الدراسة وجود علاقة خطية بين التيار المرافق للذروة وتراكيز هذه الأيونات , بينما أظهر قطب القرص الدوار حساسية أعلى تجاه التراكيز الصغيرة ضمن $\mathbf{10^{-6}}$ مول/لتر.

أيضا تم استخدام قطب القرص الدوار المغطى سطحه بطبقة من الإيثر التاجي (ثنائي بنزو-18-تاج -6) في دراسة العلاقة بين تيار الذروة والسرعة الزاوية لأيونات الفضة و النحاس.

إستخدم قطب البلاتين المغطى بطبقة من الإيثر التاجي (سالف الذكر) في التحليل الإنتزاعي لأيونات الفضة والنحاس ودلت النتائج على وجود علاقة خطية بين وقت الترسيب وتيار ذروة الإنتزاع لتلك المعادن.

إضافة إلى أنه تم إستخدام قطب البلاتين المعدل في التحليل الإنتزاعي الأنودي لأيونات الفضة والنحاس والنيكل والكادميوم وكانت نتيجة التجارب إيجابية . حيث دلت النتائج على وجود علاقة خطية بين تراكيز الأيونات سالفة الذكر وتيار ذروة إنتزاع المعدن على الفولتاموغرام ضمن

التراكيز 5×١٠^{-11} - 5×١٠^{-15} مول/لتر. وتدل هذه التجارب على أن قطب البلاتين المعدل بالإيثر التاجي يمتلك حساسية ممتازة , إنتقائية, ومدى عمل خطي واسع تجاه أيونات الفلزات.

تم قياس تركيز أيونات النحاس في سبيكة لحام بالطريقة الطيفومترية الذرية ومقارنتها بطريقة التحليل الإنتزاعي حيث أظهرت النتائج توافقا جيدا بين الطريقتين.